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Proceedings of the Sixth Annual Research Symposium

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16. ABSTRACT

The sixth annual SHWRD research symposium on management of hazardous waste was held at the Conrad Hilton Hotel in Chicago, Illinois, on March 17-20, 1980. The purpose of the symposium was two-fold: (1) to provide a forum for a state-of-the-art review and discussion of ongoing and recently completed projects dealing with the management of hazardous wastes and (2) to bring together people concerned with hazardous waste management who can benefit from an exchange of ideas and information. These proceedings are a compilation of the papers presented by symposium speakers. They are divided into two volumes representing the technologies of Treatment and Disposal. The primary technical areas covered are:

(1) Waste Sampling and Characteristics
(2) Transport and Fate of Pollutants
(3) Pollutant Control
(4) Waste Treatment and Control
(5) Pesticide Treatment and Control
(6) Co-Disposal
(7) Landfill Alternatives
(8) Remedial Actions
(9) Thermal Destruction Techniques
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FOREWORD

The Environmental Protection Agency was created because of increasing public and governmental concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of the environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is the first necessary step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and the solid and hazardous waste pollutant discharges from municipal and community sources; to preserve and treat public drinking water supplies; and to minimize the adverse economic, social, health and aesthetic effects of pollution. This publication is one of the products of that research--a vital communications link between the researcher and the user community.

These proceedings present the results of completed and ongoing research projects covering the disposal of hazardous wastes.

Francis T. Mayo
Director
Municipal Environmental
Research Laboratory

PREFACE

These proceedings are intended to disseminate up-to-date information on extramural research projects dealing with the disposal of hazardous wastes. These projects are funded by the Solid and Hazardous Waste Research Division (SHWRD) of the U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory in Cincinnati, Ohio. Selected papers from work of other organizations were included in the symposium to identify closely related work not included in the SHWRD program.

The papers in these proceedings are arranged as they were presented at the symposium. Each of the ten sessions includes papers dealing with major areas of interest for those involved in hazardous waste disposal technology.

The papers are printed here basically as received from the authors. They do not necessarily reflect the policies and opinions of the U.S. Environmental Protection Agency or Southwest Research Institute. Hopefully, these proceedings will prove useful and beneficial to the scientific community as a current reference on the disposal of hazardous wastes.

ABSTRACT

The sixth Solid and Hazardous Waste Research Division Research Symposium on treatment of hazardous waste was held at the Conrad Hilton Hotel in Chicago March 17-20, 1980. The purpose of the symposium was two-fold: (1) to provide a forum for a state-of-the-art review and discussion of ongoing and recently completed research projects dealing with the management of hazardous wastes and (2) to bring together people concerned with the disposal of hazardous waste who can benefit from an exchange of ideas and information. Bound in two volumes, Treatment and Disposal, the proceedings of the symposium are published to provide a copy of all papers in the order presented. In this document, the Disposal volume, the following seven technical areas are covered:

(1) Waste sampling and characterization
(2) Transport and fate of pollutants
(3) Pollutant control
(4) Co-disposal
(5) Landfill alternatives
(6) Remedial actions
(7) Thermal destruction techniques.

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CURRENT RESEARCH ON LAND DISPOSAL OF HAZARDOUS WASTES

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ABSTRACT

The Solid and Hazardous Waste Research Division (SHWRD), Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, in Cincinnati, Ohio, has responsibility for research in the areas of solid and hazardous waste management, including both disposal and processing. To fulfill this responsibility, the SHWRD is developing concepts and technology for new and improved systems of solid and hazardous waste management; is documenting the environmental effects of various waste processing and disposal practices; and is collecting data necessary to support implementation of processing and disposal guidelines mandated by the recently enacted Resource Conservation and Recovery Act (RCRA). This paper will present an overview of the land disposal aspects of the SHWRD hazardous waste program plan and will report the current status of work in the following categorical areas:

1. Waste Characterization/Decomposition
2. Pollutant Transport
3. Pollutant Control
4. Pollutant Treatment
5. Co-Disposal
6. Uncontrolled Sites/Remedial Action
7. Landfill Alternatives/Land Cultivation
8. Economic/Environmental Impact

INTRODUCTION

The waste residual disposal research strategy, encompassing state-of-the-art documents, laboratory analysis, bench and pilot studies, and full-scale field verification studies, is at various stages of implementation, but over the next 5 years the research will be reported as criteria and guidance documents for user communities. The waste disposal research program will develop and compile a data base for use in the development of guidelines and standards for waste residual disposal to the land as mandated by the recently enacted legislation entitled "Resource Conservation and Recovery Act of 1976" (RCRA).

The current waste residual disposal research program has been divided into three general areas: (a) Design considerations for Current Landfill Disposal Techniques; (b) Alternatives to Current Landfill Disposal Techniques; and (c) Remedial Action for Minimizing Pollutants from Unacceptable or Inoperative Sites.

The waste residual disposal research program has been discussed in previous symposiums. See Schomaker, N.B. and Roulier, M.H., Current EPA Research Activities in Solid Waste Management: *Research Symposium on Gas and Leachate from Landfills: Formation, Collection and Treatment*, March 25-26, 1975, Rutgers, State University of New Jersey; and Schomaker, N.B., Current Research on Land Disposal of Hazardous Wastes: *Residuals Management by Land Disposal: Proceedings of the Hazardous Waste Research Symposium*, February 2-4, 1976, University of Arizona; and Schomaker, N.B., Current Research on Land Disposal of Municipal Wastes: *Management of Gas and Leachate in Landfills: Proceedings of the Third Annual Municipal Solid Waste Research Symposium* March 14-16, 1977, University of Missouri, and Schomaker, N.B., Current Research on Land Disposal of Hazardous Wastes: *Proceedings of the Fourth Annual Research Symposium* March 6-8, 1978, Southwest Research Institute and Schomaker, N.B.

Current Research on Land Disposal of Municipal Solid Wastes: Land Disposal: *Proceedings of the Fifth Annual Research Symposium* March 26-28, 1979, University of Central Florida.

WASTE CHARACTERIZATION/DECOMPOSITION

The overall objective of this research activity is to provide information on the composition of municipal and hazardous wastes, the compatibility of hazardous wastes, and aqueous and gaseous emissions from disposed wastes. Sampling techniques, analytical methods, and techniques for determining emissions will be developed for implementing better disposal practices and waste management.

The initial effort (1) in the hazardous waste characterization area relates to the chemical composition, physical characteristics, and origin of hazardous wastes delivered to several Class I (hazardous chemical) landfills in the State of California. The average concentration, estimated daily decomposition, and partitioning of 17 metal species in hazardous waste landfills in the greater Los Angeles, California area was studied. Mass deposition rates were determined by calculating the average concentration of the metal species in conjunction with approximate daily volume received at the site. The effort has been published in a report entitled *A Case Study of Hazardous Wastes Input Into Class I Landfills* - EPA-600/2-78-064, June 1978.

Standard Sampling Techniques

Standard Sampling procedures, including collection, preservation, and storage of samples, do not exist for solid and semi-solid wastes. Hazardous wastes, both at the point of generation and the point of disposal, are not homogenous mixtures and, additionally, may range in consistency from a liquid, through a pumpable sludge, to a nonpumpable solid. Existing procedures for sampling liquid effluents and soils will have application but must be adapted to a variety of circumstances and, more importantly, field tested extensively before they can be advocated as "the" way to sample. Experience with sampling procedures is being accumulated as part of several on-going SHWRD projects.

The initial effort (1) in this sampling technique area relates to an activity for standardized methods for sampling and analysis of hazardous wastes. Specialized sampling methods have been developed for safe, reproducible, and representation sampling of such wastes in a wide variety of physical states, compositions, and locations. Methods of containment, handling and custody of waste samples have also been investigated. This effort is being published in a report entitled *Samplers and Sampling Procedures for Hazardous Waste Streams* - EPA 600/2-80-018, January 1980. This effort has been expanded to include development of a list of reactive, wastes and test methods for those wastes thought to cause serious problems.

Standard Analytical Techniques

Analysis of the contaminants within a waste leachate sample is difficult due to interfering agents. Existing instrumentation functions well in the analysis of simple mixtures at moderately low concentrations but intereference problems can be encountered for complex mixtures at high concentrations (1 percent by weight and greater). In this range the sample cannot always be analyzed directly and commonly must be diluted and/or analyzed by the method of standard additions. Options are the development of standard procedures for diluting and accounting for errors introduced thereby or the development of instrumentation capable of accurate, direct measurements at high concentrations in the presence of potential multiple interferences. Existing USEPA procedures for water and wastewaters are often not applicable. Analytical procedures are being developed on an as-needed basis as part of the SHWRD projects. However most of this work is specific to the wastes being studied and separate efforts were required to insure that more general procedures/equipment would be developed.

The initial effort (2) relates to the compilation and evaluation of current leaching tests methods. In this study various available leaching tests are described and the methods utilized are evaluated in relation to their adaptability to field conditions. Also, as a part of the sampling technique activity, analysis of wastes has been developed as a four level scheme, which begins with field characterization followed by three levels of progressively more detailed and instrument intensive laboratory analysis. The results of this effort are discussed in a report entitled *Compilation and Evaluation of Leaching Test Methods*, EPA-600/2-78-095, May 1978.

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(1) Parenthesis numbers refer to the project officers, listed immediately following this paper, who can be contacted for additional information.

A second effort (2) will determine which sampling and preservation techniques should be accepted as standards for groundwater sampling. Other objectives of the study are to determine if current sampling methods produce samples representative of water contained in the aquifer being monitored and if groundwater samples collected in the field can be treated on location or if laboratory treatment is required. Six landfill monitoring wells will be studied using four different pumping techniques and thirteen different sample preservation procedures.

A third effort (2), is an in-house activity to determine the capability of existing analytical procedures to quantitate priority pollutants in various waste landfill leachates. Preliminary efforts will obtain leachates from four landfill sites, two municipal solid wastes and two hazardous waste sites, to determine specific priority pollutants. Data will be analyzed to resolve analytical methodology applicable to leachate samples.

Standard Leaching Tests

In studying the potential environmental impact of contaminants, a standard leaching test is needed to assess contaminant release from a waste. Such a test must provide information on the initial release of contaminants from a waste contacted not only by water but also by other solvents that could be introduced in disposal. Additionally, such a test must provide some estimate of the behavior of the waste under extended leaching.

Validation of a Standard Leaching Test (SLT) was the initial effort funded in part by SHWRD (2). Existing leaching tests were evaluated for those elements that were of special benefit to the development of an SLT. This information has been published in a report described in the "Standard Analytical Techniques" section above. Three candidate SLT's were chosen for further testing. The additional effort has been published in two reports entitled *Comparison of Three Waste Leaching Tests, Executive Summary*, EPA-600/8-79-001, May 1979 and *Comparison of Three Waste Leaching Tests*, EPA-600/2-79-071, July 1979. Also a *Newsletter, Solid Waste Brief*, May 1979, dedicated to the rapid/dissemination of information relative to solid waste "Extraction Procedure" (EP) portion of Section 3001 of RCRA has been published (2).

A second effort (2) has been identified as the "Extraction Procedure" (EP) test will establish a data base on toxicity of leachates from wastes and establish recommended toxicity of leachates from wastes and establish recommended toxicity test protocols in order to establish criteria defining acute and/or chronic hazardous wastes. Work has been initiated on four waste categories: municipal refuse, Chicago sewage sludge, arsenic sludge and power industry residuals.

Waste Leachability

The characteristics of leachates from hazardous wastes are being investigated in several different studies. The initial hazardous waste leaching effort (4) was patterned after a method developed by the (I.A.E.A.) for leach testing immobilized radioactive waste solids. This effort has been published in a report entitled *Elutriate Test Evaluation of Chemically Stabilized Waste Materials* - EPA-600/2-79-154, August 1979. Translucent plexiglass columns were utilized and observations of flow patterns as well as possible biological activity were made. Five industrial sludges and five Flue Gas Desulfurization (FGD) sludges were investigated. This effort is basically completed and the final report is being prepared. An interim report entitled *Pollutant Potential of Raw and Chemically Fixed Hazardous Industrial Wastes and Flue Gas Desulfurization Sludges*, EPA-600/2-75-182, July 1975, has been published.

Another on-going waste leachability effort (5) relates to inorganic industrial waste where there is no appreciable biological activity. This testing program was designed to evaluate leaching and pollutant release under a variety of leaching conditions which may be encountered in one or more disposal situations and to develop a short-term leaching and soil interaction test. Five different types of leaching conditions were utilized which employed three varying pH leaching fluids, deionized water and municipal refuse leachate. A major consideration in the leaching behavior of wastes is time. Some wastes will not release appreciable amounts of contaminants until leaching has removed salinity or reserve alkalinity from the waste. Accordingly, the laboratory leaching test is extended over time. Successive extracts of a waste, which change in composition as the waste is depleted, are used to challenge a sequence of three soil batches that are graded in size to allow taking samples for analysis between each step and to compensate for extract absorbed by the soil. The laboratory leaching procedure allows simulating one to ten years of field leaching and soil interaction in about two weeks of laboratory extractions. The test has not yet been checked against field data.

POLLUTANT TRANSPORT

Pollutant transport studies involve the release of pollutants in liquid and gaseous forms from various municipal and hazardous wastes and the subsequent movement and fate of these pollutants in soils adjacent to disposal sites. Both laboratory and field verification studies at selected sites are being performed to assess the potential for groundwater contamination. The studies will provide the information required to (a) select land disposal sites that will naturally limit release of pollutants to the air and water and (b) make rational assessments of the need for and cost-benefit aspects of leachate and gas control technology.

The overall objective of this research activity is to develop procedures for using soil as a predictable attenuation medium for pollutants. Not all pollutants are attenuated by soil, and in some cases, the process is one of delay so that the pollutant is diluted in other parts of the environment. Consequently, a significant number of the research projects funded by SHWRD are focused on understanding the process and predicting the extent of migration of contaminants (chiefly heavy metals) from waste disposal sites.

These pollutant migration studies are being performed simultaneously in the areas of hazardous wastes and municipal refuse. Several previous discussions of these efforts have been presented. See Roulier, M.H., *Attenuation of Leachate Pollutants by Soils*, presented at the *Management of Gas and Leachate in Landfills: Proceedings of the Third Annual Municipal Solid Waste Research Symposium*, March 14-16, 1977, University of Missouri.

Bibliography and State of the Art

The initial effort (4) in this area resulted in a completed bibliography entitled, A *Bibliography, Volume 1: Selected Metals* EPA-600/9-79-024a, August 1979, and *Volume 2: Pesticides* EPA-600/9-79-024b, August 1979.

A second effort (4) consisted of a review of information on migration through soil of potentially hazardous pollutants contained in leachates from waste materials. The results have been published in a report entitled *Movement of Selected Metals, Asbestos, and Cyanide in Soils: Applications to Waste Disposal Problems*, EPA-600/2-77-022, April 1977. The document presents a critical review of the literature pertinent to biological, chemical, and physical reactions, and mechanisms of attenuation (decrease in the maximum concentration for some fixed time as distance traveled) of the selected elements arsenic, beryllium, cadmium, chromium, copper, iron, mercury, lead, selenium, and zinc, together with asbestos and cyanide, in soil systems.

Controlled Lab Studies

The initial effort (4) examined the factors that attenuate contaminants (limit contaminant transport) in leachate from municipal solid waste landfills. These contaminants are: arsenic, beryllium, cadmium, chromium, copper, cyanide, iron, mercury, lead, nickel, selenium, vanadium, and zinc. The general approach was to pass municipal leachate as a leaching fluid through columns of well characterized, whole soils maintained in a saturated anaerobic state. The typical municipal refuse leachate was spiked with high concentrations of metal salts to achieve a nominal concentration of 100 mg/l. The most significant factors in contaminant removal were then inferred from correlation of observed migration rates and known soil and contaminant characteristics. This effort will contribute to the development of a computer simulation model for predicting trace element attenuation in soils. Modeling efforts to date have been hindered by the complexity of soil-leachate chemistry. The results of this effort have been published in a report entitled *Investigation of Landfill Leachate Pollutant Attenuation by Soils* EPA-600/2-78-158, August 1978.

The second effort (4) in this area studied the removal of contaminants from landfill leachates by soil clay minerals. Columns were packed with mixtures of quartz sand and nearly pure clay minerals. The leaching fluid consisted of typical municipal refuse leachate without metal salt additives. The general approach to this effort was similar to that described in the preceding effort except that (a) both sterilized and unsterilized leachates were utilized to examine the effect of microbial activity on hydraulic conductivity and (b) extensive batch studies of the sorption of metals from leachate by clay minerals were conducted. The results of this effort have been published in a report entitled *Attentuation of Pollutants in Municipal Landfill Leachate by Clay Minerals*, EPA-600/2-78-157 August 1978.

The third effort (5) relates to modeling movement in soils of the landfill gases, carbon dioxide and methane. The modeling movement has been verified under laboratory conditions. This effort has not focused on the impact of gases on groundwater, but considers groundwater as a sink for carbon dioxide. Results to date have evaluated efficiency of vertical chimney vents, barriers and forced convection systems.

A fourth effort (4) relates to the use of large-scale, hydrologic simulation modeling as one method of predicting contaminant movement at disposal sites. The two-dimensional model that was used successfully to study a chromium contamination problem is being developed into a three-dimensional model and will be tested on a well-monitored landfill where contaminant movement has already taken place. Although this type of model presently needs a substantial amount of input data, it appears promising for determining contaminant transport properties of field soils and, eventually, predicting contaminant movement using a limited amount of data.

A fifth effort (1) relates to organic contaminant attenuation by soil. This is our initial effort in organic contaminant movement in soil. Much more is known about inorganic contaminant movement in soil because the analytical techniques for inorganic materials are well developed and relatively cheap compared to the time-consuming analytical techniques for organic materials. The problem is compounded by the fact that organic contaminants are more numerous and more are being synthesized all the time. PCB is the organic contaminant currently being investigated. As a part of the above described effort, a gas chromatographic analytical procedure was developed that allowed improved quantitative measurement of PCB's in aqueous solutions. The initial results of this study is currently being published in a report entitled *Attenuation of Wastes Soluble PCB's by Earth Materials.*

A sixth effort (4) relates to an evaluation of the conditions that would control the movement of hexachlorobenzene (HCB) out of landfills and other disposal/storage facilities into the surrounding atmosphere. The potential for volatilization indicates a need for disposal site coverings that will reduce the vapor phase transport of HCB into the surrounding atmosphere. The volatilization fluxes of hexachlorobenzene from industrial wastes (hex waste) were determined using coverings of soil, water and polyethylene film in a simulated landfill under controlled laboratory conditions. Coverings of water and soil were found to be highly efficient when compared on a cost basis. Volatilization flux through a soil cover was directly related to soil air-filled porosity and was therefore greatly reduced by increased soil compaction and increased soil water content.

A seventh effort (4) relates to the adsorption, movement and biological degradation of high concentrations of pesticides in soils. Equilibrium adsorption isotherms were obtained for 2,4-D amine, atrazine, terbacil, and methyl parathion and four soils from different locations within the United States. Pesticide solution concentrations ranged from zero to the aqueous solubility limit of each pesticide. The mobility of each pesticide increased as its concentration in the soil solution phase increased. Pesticide degradation rates and soil microbial populations generally declined as the pesticide concentration in the soil increased. The results of this effort will be published in a report entitled *Adsorption, Movement and Biological Degradation of Large Concentrations of Selected Pesticides in Soils.*

An eighth effort (4) was recently initiated to determine how accurately the EPA Gas Movement Model predicts the maximum distance that methane gas will move through soils adjacent to landfills and how accurately this model will predict the relative effectiveness of control systems (e.g., trenches, wells, barriers) for minimizing methane gas movement.

A ninth (4) effort relates to the influence of chemicals on the permeability of clay soils. The objective is to develop a guidance manual identifying wastes that increase the permeability of soils at a disposal site. The study will also develop a test procedure for predicting whether a specific waste and soil will react to increase the permeability.

A tenth (4) effort relates to the determination of the attenuation mechanisms and capacity of selected clay minerals and soils for hexachlorocyclopropentadial (HCCPD) and "hex" wastes. Also effects of caustic-soda brine on the attenuation and solubility of HCCPD and the development of a chemical model to predict HCCPD migration through soil will be pursued. Except for the measurement of the salting coefficient of HCCPD, the approach will be the same as described in the fifth effort listed above.

Field Verification

Limited field verification is being conducted. The initial effort (3) to date has consisted of installing monitoring wells and coring soil samples adjacent to three municipal landfill sites to identify contaminants and determine their distribution in the soil and groundwater beneath the landfill site. The sites represent varying geologic conditions, recharge rates, and age, ranging from a site closed for 15 years to a site currently operating. Individual site characteristics were identified, and sample analyses necessary to determine the primary pollutant levels in the waste soils and groundwater were determined. The results of this effort are discussed in a report entitled *Chemical and Physical Effects of Municipal Landfills on Underlying Soils and Groundwater*, EPA-600/2-78-096, May 1978.

A second effort (4) relates to the vertical and horizontal migration patterns, of zinc, cadmium, copper, and lead through the soil and shallow aquifer systems at a secondary zinc smelter. These patterns were defined using soil coring and monitoring well techniques. The migration of metals that occurred has been limited to relatively shallow depths into the soil profile by attenuation processes. Soil coring was determined to be an effective investigative tool, but not suitable by itself for routine monitoring of waste disposal activities. However, it should be used to gather preliminary information to aid in determining the proper horizontal and vertical locations for monitoring well design. The results from this study are currently being published in a report entitled *Field Verification of Toxic Wastes Retention by Soils at Disposal Sites.*

POLLUTANT CONTROL

Pollutant control studies are needed because experience and case studies have shown that some soils will not protect groundwater from contaminants. Even sites with "good soils" may have to be improved to protect against subsurface pollution. The overall objective of this research activity is to lessen the impact of pollution from waste disposal sites by technology that minimizes, contains, or eliminates pollutant release and leaching from waste residuals disposed of to the land.

The pollutant control studies are determining the ability of in-situ soils and natural soil processes to attenuate leachate contaminants as the leachate migrates through the soil from landfill sites. The studies are also determining how various synthetic and admixed materials may be utilized as liners to contain and prevent leachates from migrating from landfill sites.

Natural Soil Processes

The treatment by natural soil processes of pollutants from hazardous waste and municipal refuse disposal sites is being performed in the controlled lab studies previously discussed in the section on pollutant transport.

Liners/Membranes/Admixtures

The liner/membrane/admixture technology (3) is being studied to evaluate suitability for eliminating or reducing leachate from landfill sites of municipal or industrial hazardous wastes. The test program will evaluate, in a landfill environment, the chemical resistance and durability of the liner materials over 12- and 36-month exposure periods to leachates derived from industrial wastes, SO_x wastes, and municipal solid wastes. Acidic, basic, and neutral solutions will be utilized to generate industrial waste leachates.

The liner materials being investigated under the hazardous waste program include five admixed materials and eight polymeric membranes. The admixed materials are:

- Asphalt emulsion or nonwoven fabric (0.3 in)
- Compacted native fine-grain soil (12.0 in)
- Hydraulic asphalt concrete (2.5 in)
- Modified bentonite and sand (5.0 in)
- Soil cement with and without surface seal (4.0 in)

The eight polymeric membrane liners are:

- Butyl rubber, fabric reinforced (34 mils)
- Chlorinated polyethylene (32 mils)
- Chlorosulfonated polyethylene, fabric reinforced (34 mils)
- Elasticized polyolefin (20 mils)
- Ethylene propylene rubber (50 mils)
- Neoprene, fabric reinforced (32 mils)
- Polyester elastomer, experimental (8 mils)
- Polymeryl chloride (30 mils)

Specimens of these materials have been exposed for more than 3 years to the following six classes of hazardous wastes which utilized ten specific types of wastes: strong acid; strong base; waste of saturated and unsaturated oils; lead waste from gasoline tanks; oil refinery tank bottom waste (aromatic oil); and pesticide waste.

Preliminary exposure tests have been completed on the various liner materials in the various wastes in order to select combinations for long term exposures. The results of these tests along with a discussion of the overall hazardous waste liner material program are presented in a report entitled *Liner Materials Exposed to Hazardous and Toxic Sludges First Interim Report*, EPA-600/2-77-081, June 1977.

A second effort (3) relates to a state-of-the-art of landfill impoundment techniques. The literature search surveyed the use of liner materials in impoundment sites for the containment of seven general types of industrial wastes. This data was supplemented with information obtained from various manufacturers, suppliers and installers and contains analyses of liner compatibility with industrial wastes.

The results of this effort have been published in a report entitled, *State-of-the-Art Study for Landfill Impoundment Techniques*, EPA-600/2-78-196, Dec. 1978.

A third effort (3) relates to the types of materials being tested for use as liners for sites receiving sludges generated by the removal of sulfur oxides (SO_x) from flue gases of coal-burning power plants. The volumes of SO_x sludge generated in any particular place will, typically, be much greater than those for other types of wastes, and therefore the disposal sites will be large. Consequently, methods of lining such disposal sites must have a low unit cost. It is desirable that materials be easy to apply or install. Because of these considerations, the number of polymeric membranes included in the study have been reduced whereas admixed and sprayed-on materials are being emphasized. A total of 18 materials are being tested with two types of Flue Gas Desulfurization (FGD) sludges. The sludges are from an eastern coal lime and limestone scrubbed process.

The liner materials consisted of admixed material, prefabricated membranes, and spray on materials. The admixed materials consisted of the following: cement; lime; cement with lime, polymeric bentonite blend (M179); gray powder-quartec (UF); asphaltic concrete; TACSS 020; TACSS 025; TACSS C400; and TACSS ST. The prefabricated membranes liner materials consisted of the following: elasticized polyolefin; black neoprene - coated nylon; and black neoprene - reinforced fabric. The spray-on liner materials consisted of the following: polyvinyl acetate; natural rubber latex; natural latex; polyvinyl acetate;

asphalt cement; and molten sulphur. For this above effort, a total of 72 special test cells were constructed to perform 12 and 24 month exposure tests. The final report is entitled *Flue Gas Cleaning Sludge Leachate/Liner Compatibility Investigated: Interim Report*, EPA-600/2-79-136, Aug. 1979.

A fourth effort (3) relates primarily to the identification and description of waste disposal sites and holding ponds which have utilized an impermeable lining material. Also, three potential excavation techniques for liner recovery operations are described and discussed. This effort has been published in a report entitled *Liners for Sanitary Landfills and Chemical and Hazardous Waste Disposal Sites* EPA-600/9-78-005, May 1978.

A fifth effort (3) relates to a study to assess actual field procedures utilized in (1) preparing the supporting subbase soil structure for liners and (2) placing the various liner materials common to projects requiring positive control of fluid loss. In addition, problems and solutions will be identified which can be avoided by proper preplacement and placement procedures. To perform this study, a study team provided with a checklist, obtained from manufacturer's recommendations for placement, are visiting a variety of liner installation projects to observe first-hand the placement construction and procedures actually used to place the linings. Differences between the recommended practices and the actual procedures used, if any, will be questioned and reviewed with the placement contractor.

Chemical Stabilization

Chemical stabilization is achieved by incorporating the solid and liquid phases of the waste into a relatively inert matrix which is responsible for increased physical strength and which protects the components of the waste from dissolution by rainfall or by soil water. If this slows the rate of release of pollutants from the waste sufficiently so that no serious stresses are exerted on the environment around the disposal site, then the wastes have been rendered essentially harmless and restrictions on where the disposal site may be located will be minimal.

The initial chemical fixation effort (3) relates to the transforming of the waste into an insoluble or very low solubility form to minimize leaching. The test program consists of investigating ten industrial waste streams, both in the raw and fixed state. The waste streams were treated with at least one of seven separate fixation processes and subjected to leaching and physical testing.

The lab and field studies have been completed. The laboratory leaching test data for the first six months includes: methods for physical and chemical analyses, documentation of various sludge fixation processes, and physical and chemical data on the sludges. The results have been compiled and discussed in a report entitled *Pollutant Potential of Raw and Chemically Fixed Hazardous Industrial Wastes and Flue Gas desulfurization Sludges - Interim Report*, EPA-600/2-76-182, July 1976.

The laboratory physical program test included physical properties (grain size distribution, atterbug limits, specific gravity, volume-weight-moisture relationships and permeabilities), engineering properties (compaction and unconfined compression) and durability properties (wet-dry and freeze-thaw) for both the raw and fixed sludges. The results of this effort have been discussed in a report entitled, *Physical and Engineering Properties of the Hazardous Industrial Wastes and Sludges*, EPA-600/2-77-139, August 1977.

The second effort (3) relates to a survey and identification of solidification/stabilization technology available in addition to those techniques currently being investigated. This effort consisted of examining six major categories of industrial waste fixation systems and discussing the advantages/disadvantages of each. The six categories are shown below:

- o Cement - based techniques
- o Lime - based techniques
- o Thermoplastic techniques (including bitumen, paraffin and polyethylenes)
- o Organic polymer techniques
- o Self-cementing techniques

Another aspect of this effort consisted of listing and describing some 13 companies that solidify or fix hazardous wastes or sell fixation materials. The survey and identification have been completed and the results have been published in a report entitled *Survey of Solidification/Stabilization Technology for Hazardous Industrial*

Wastes, EPA-600/2-79-056, July 1979.

The third effort (3) relates to a series of field verification studies to verify success and which pollutants have been immobilized at landfills receiving stabilized hazardous wastes. Four sites where stabilized industrial wastes and three sites where stabilized flue gas cleaning sludges had been disposed were examined to determine the effects of stabilized wastes on surrounding soils and groundwater. The sludges had all been fixed using the same proprietary process. Two of the industrial waste sites contained auto assembly (metal finishing wastes, one site contained electroplating wastes and the fourth site contained refinery sludges. The physical properties of soils under the disposal sites were affected little, if at all, by the disposal operation. The results are reported in the publication entitled *The Effects of Flue Gas Cleaning Waste on Groundwater Quality and Soil Characteristics*, EPA-600/2-79-164, August 1979.

A fourth effort (2) relates to a laboratory assessment of fixation and encapsulation processes for arsenic-laden wastes. Three industrial solid wastes that are high in arsenic concentration have been treated by generic processes in laboratory and by proprietary processes at vendors' facilities. Leaching studies on treated wastes consisting of Shake tests on pulverized samples and on intact monolithic samples are being performed to assess the relative safety of each product for disposal.

A fifth effort (6) relates to encapsulating process for managing hazardous wastes. This study consists of developing and evaluating techniques for encapsulating hazardous wastes. Techniques for encapsulating unconfined dry wastes are discussed in a report entitled *Development of a Polymeric Cementing and Encapsulating Process for Managing Hazardous Wastes*, EPA-600/2-77-045, August 1977. Additional evaluations are currently being performed whereby containers of hazardous waste (i.e., 55 gallon drums) are placed in a fiber glass thermo-setting resin casing and the casing is covered with a high density polyethylene. Laboratory tests are being performed: to evaluate stresses encountered during storage, transport and disposal in a landfill; to leaching by water and HCL, and to mechanical tests to evaluate the ability to retain toxic materials. Also being evaluated is the use of cements for encapsulation of small containers.

Moisture Infiltration

The initial effort (3) involves the identification of the functional requirements of cover soil and the ability of various soil types to meet these requirements. Of primary interest is the minimization of moisture infiltration through landfill cover soils. Other criteria associated with landfill cover soils, i.e., infiltration, gas venting, vegetation, soil erosion, rodent burrowing trafficability will also be identified. The characteristics of the various soil types are reviewed individually and in combination with other soil types to determine the most suitable type of cover material for use in meeting the desired functional requirements for a given disposal site. The initial results from this study have been published in a report entitled *Cover for Solid Waste Landfills: Considerations for Design and Construction*, EPA-600/2-79-136, Aug. 1979.

POLLUTANT TREATMENT

The overall objective of the pollutant treatment studies is to develop chemical, physical, and biological processes for treating landfill leachate once it has been collected and contained at the landfill site. Treatment by natural soil processes may be used at some sites where pollutant retention by soils is sufficient to allow uncontrolled release of leachate from the landfill into underlying soils.

Natural Soil Processes

The treatment of pollutants (4) from hazardous waste and municipal refuse disposal sites by natural soil processes has been described previously in the section on pollutant transport.

Physical-Chemical Treatment

The treatment of municipal refuse leachate (5) was evaluated in several laboratory studies using the following physical-chemical processes: chemical precipitation, activated carbon adsorption, and chemical oxidation. This study discussed in two reports entitled *Evaluation of Leachate Treatment: Volume I - Characteristics of Leachate*, EPA-600/2-77-186a, September 1977 and *Evaluation of Leachate*

Treatment: Volume I - Characteristics of Leachate, EPA-600/2-77-186a, September 1977 and *Evaluation of Leachate Treatment: Volume II - Biological and Physical-Chemical Processes*, EPA-600/2-77-186b, Nov. 1977.

A second effort (4) relates to a laboratory study of agricultural limestone and hydrous oxides of Fe. This study was performed to evaluate their use as landfill liner materials to minimize the migration of metal contaminants. Preliminary research on limestone and Fe hydrous oxide liners indicates these materials have a marked retarding influence on many of the trace elements. The limestone barrier showed the migration rate of all 12 metals studied and it was more effective in retention of some metals than others. However, the increased water contamination from solubilization of iron seems to rule out use of iron oxides until further work is conducted.

A third effort (4) relates to a laboratory evaluation of ten natural and synthetic materials (bottom ash, flyash, vermiculite, illite, Ottawa Sand, activated aluminia, cullite) for the removal of contaminants in the leachate and liquid portion of three different industrial sludges (calcium fluoride sludge, petroleum sludge, metal finishing sludge). Results of the laboratory experiments indicate sorbent capacity is a function of the pH and concentration of the particular contaminant in the leachate with the volume of leachate that can be treated with maximum removal being regulated by the velocity through the bed. The information discussed in a report entitled *Sorbents for Fluoride, Metal Finishing and Petroleum Sludge Leachate Contaminant Control*, EPA-600/2-78-024, March 1978.

Biological Treatment

Various unit processes for biological treatment have been investigated in the laboratory for only municipal refuse leachates. This effort (5) has investigated the process kinetics, the nature of the organic fraction of municipal refuse leachate, and the degree of treatment that may be obtainable using conventional wastewater treatment methods. The biological methods evaluated were the aerobic filter, the aerated lagoon, and combined treatment of activated sludge and municipal sewage. Biological units were operated successfully without prior removal of the metals that were present in high concentrations. The results of this effort are discussed in the same two EPA leachate treatment reports mentioned under the above physical/chemical treatment section.

CO-DISPOSAL

The overall objective of the co-disposal activity is to assess the impact of the disposal of industrial waste materials with municipal solid waste. Concern has been voiced that the addition of industrial waste may result in the occurrence of various toxic elements in leachates and thereby pose a threat to potable groundwater supplies. Because the environmental effects from landfilling result from not only the soluble and slowly soluble materials placed in the landfill but also the products of chemical and microbiological transformations, these transformations should be a consideration in management of a landfill to the extent that they can be predicted or influenced by disposal operations.

The initial effort (5) involves a study of the factors influencing (1) the rate of decomposition of solid waste in a sanitary landfill, (2) the quantity and quality of gas and leachate produced during decomposition, and (3) the effect of admixing industrial sludges and sewage sludge with municipal refuse. A combination of municipal solid waste and various solid and semi-solid industrial wastes was added to several field lysimeters. All material flows were measured and characterized for the continuing study and related to leachate quality and quantity, gas production, and microbial activity.

The industrial wastes investigated were: petroleum sludge, battery production waste, electroplating waste, inorganic pigment sludge, chlorine production brine sludge, and a solvent-based paint sludge. Also, municipal digested primary sewage sludge dewatered to approximately 20 percent solids was utilized at three different ratios. The results of this initial effort have been reported in a paper entitled *The Effects of Industrial Sludges on Landfill Leachate and Gas, Proceedings - National Conference on Disposal of Residues on Land*, September 1976, pp. 69-76. The updated results of this effort is being published in a report entitled *Pilot Scale Evaluation of Sanitary Land-*

filled Municipal and Industrial Wastes.

A second effort (4) to assess the potential effects of co-disposal involves the leaching of industrial wastes with municipal landfill leachate as well as water. Leachate from a municipal solid waste (MSW) landfill was used to extract the five industrial wastes and to study movement of their components in the soil columns. MSW leachate dissolved much greater amounts of substances from the wastes and apparently increased the mobility of these substances in the soil columns relative to the dissolution and mobility observed when deionized water was used as a leaching solution. The municipal landfill leachate is a highly odorous material containing many organic acids and is strongly buffered at a pH of about 5. Consequently, it has proved to be a very effective solvent. A sequential batch leaching and soil adsorption procedure has been developed that provides information comparable to that from soil column studies but in a much shorter time.

A third effort (4) relates to chemically treated and untreated industrial wastes being disposed of in a simulated municipal refuse landfill environment. Large lysimeters, six foot in diameter by twelve feet high, are being utilized to determine the difference in leachate quality between the treated and untreated wastes when mixed with municipal refuse. The industrial sludges selected for the study were calcium fluoride, chlorine brine production and electroplating. The sludges were chemically fixed by two processors. The material was allowed to cure as per the processors' recommendations. Leaching data will be correlated with the laboratory leaching data to determine the benefits of co-disposing of treated wastes.

UNCONTROLLED SITES/REMEDIAL ACTION

An ongoing study by OSW has identified incidents of well contamination due to waste disposal sites. Seventy-five to 85 percent of all sites investigated are contaminating ground or surface waters. In order to determine the best practical technology and economical corrective measures to remedy these landfill leachate and gas pollution problems, a research effort has been initiated (2) to provide local municipalities and users with the data necessary to make sound judgments on the selection of viable, in-situ, remedial procedures and to give them an indication of the cost that would be associated with such a project. This research effort is being pursued at a municipal refuse landfill site at Windham, Connecticut. The site was selected from a candidate site list of 17 which took into account appropriate site selection criteria. This effort consists of three phases. Phase I will be an engineering feasibility study that will determine on a site specific basis the best practicable technology to be applied from existing neutralization or confinement techniques. Phase II will determine the effectiveness, by actual field verification, of the recommendations/first phase study. Phase III will provide a site remedial guide to local municipalities and users. The engineering feasibility study has been completed and a report entitled *Guidance Manual for Minimizing Pollution from Waste Disposal Sites*, EPA-600/2-78-142, August 1978 has been published. This guidance document emphasizes remedial schemes or techniques for pollution containment. The remedial schemes discussed in this document are:

- Surface Water Control
  - o surface sealing
  - o revegetation
- Groundwater Control
  - o bentonite slurry-trench cutoff wall
  - o grout curtain
  - o sheet piling cutoff wall
  - o bottom sealing
- Plume Management
  - o extraction
  - o injection
  - o leachate handling
- Chemical Immobilization
  - o chemical fixation
  - o chemical injection
- Excavation and Reburial

The scheme currently installed and monitored for the Connecticut MSW site is a surface capping technique which could be followed by a leachate extraction scheme if required.

LANDFILL ALTERNATIVES/LAND CULTIVATION

Waste materials are primarily deposited in sanitary landfills or incinerated. Because of concern for environmental impact and economics, other landfill alternatives have been proposed. For SHWRD purposes, the alternatives currently being considered are: (1) deep well injection, (2) underground mines, and (3) land spreading. The overall objective of the landfill alternatives study is to determine the feasibility and beneficial aspects of these techniques by assessing the environmental impact and economics.

Deep Well Injection

The first effort (7) consisted of a review and analysis of available information related to deep-well injection, and an assessment as to the adequacy of this method for managing hazardous wastes and ensuring protection of the environment. The study provided a comprehensive compilation of available information regarding the injection of industrial hazardous waste into deep wells. This effort has been discussed in a four volume report entitled *Review and Assessment of Deep-Well Injection of Hazardous Waste, Volumes I-IV*, EPA-600/2-77-029 (a-d), June 1977.

A second effort (5) provided detailed information on the application of deep well injection technology. Local geologic and hydrologic characteristics of the injection and confining intervals are considered along with the physical, chemical and biological compatibility of the receiving zone with the wastewater to be injected. Design and construction aspects of injection wells are presented along with recommended preinjection testing, operating procedures, and emergency precautions. This effort is discussed in a report entitled *An Introduction to the Technology of Subsurface Wastewater Injection*, EPA-600/2-77-240, December 1977.

Underground Mines

The initial effort (7) consisted of a review and analysis of information of the placement of hazardous waste in mine openings. The study assessed the technical feasibility of storing nonradioactive hazardous wastes in underground mine openings. The results showed that a majority of the wastes considered can be stored underground in an environmentally acceptable manner if they are properly treated and containerized. This effort is discussed in a report entitled *Evaluation of Hazardous Waste Emplacement in Mixed Openings*, EPA-600/2-75-040, December 1975.

A second effort (4) related to an economic evaluation of storing nonradioactive hazardous wastes in a typical room and pillar type salt mine. The results include capital and operating costs and a cost analysis. The cost study was based on a simulated waste characteristic and conceptual design of the waste receiving, treatment, containerization, and underground storage facilities. This effort is discussed in a report entitled *Cost Assessment for the Emplacement of Hazardous Materials in a Salt Mine*, EPA-600/2-77-215, November 1977.

Land Cultivation

The disposal technique of land cultivation, whereby specific waste residues have been directly applied or admixed into soils, has been an alternate disposal option for many years by pharmaceutical, tannery, food processing, paper and pulp, and oil refinery industries. The soil environment can assimilate most types of organic waste by processes of adsoprtion, dilution, biodegradation, and oxidation. The initial effort (4) relates to gathering and assessing available information on land cultivation of hazardous industrial sludges with emphasis on characterization of waste types, quantities, operational technology, economics and environmental impacts. The results of this initial effort are discussed in two reports entitled *Land Cultivation of Industrial Wastes and Municipal Solid Wastes: State-of-the-Art Study, Volume I - Technical Summary and Literature Survey*, EPA-600/2-78-140a, August 1978 and *State-of-the-Art Study, Volume II - Field Investigation and Case Studies*, EPA-600/2-78-140b August 1978.

The second effort (4) is a combination laboratory, greenhouse and field study to determine the fate and mobility of wastes in soil for the purpose of developing criteria for use in the design, management and monitoring of land cultivation disposal operations. Decomposition rate, application rate, plant survival and growth, pollutant runoff and leachate generation will be obtained in development of the data base.

The third effort (4) relates to detailed field surveys and limited laboratory field experimentation for the purpose of developing a matrix of industrial organic and inorganic and municipal waste streams versus operational parameters. This matrix of information will be used to develop design and guideline criteria.

The fourth effort (8) relates to the pit disposal method for excess pesticides as generated by farmers and agricultural applicators. Experimental systems have been developed to investigate the fate of selected pesticides in isolated micro-pits under controlled conditions. The chemical and biological consequences of pit disposal of dilute insecticides, fungicides, and rodenticides are being determined. The initial results of the study are described in a report entitled *State-of-the-Art Report: Pesticide Disposal Research*, EPA-600/2-78-183, August 1978.

ECONOMIC/ENVIRONMENTAL IMPACT

The use of market-oriented incentive (disincentive) mechanisms has received very scant consideration for pollution control policy in the United States, particularly in the area of hazardous waste management. Economic theory suggests that incremental pricing of waste collections and disposal would reduce the waste generation rate, enhance source separation of recyclable materials, accelerate technological innovation, and minimize total system cost.

The economic relevance is being addressed to hazardous waste management in general and the environmental impact aspect is being addressed to Flue Gas Cleaning (FGD) sludge disposal.

In the economic relevance effort (8) currently being investigated, a methodology is being developed that permits economic and social impacts of alternative approaches to hazardous waste management to be addressed. The procedure involves generation of a series of environmental threat scenarios that might arise from the use of different hazardous waste management techniques. The costs attributable to any technique comprise the control costs, and the environmental costs and benefits together determine the net benefits associated with the threat scenarios. This effort has been received in draft report form for processing into a final report entitled *Economic Analysis of Hazardous Waste Management Alternatives: Methodology and Demonstration.*

In the environmental impact effort (2) the problem of FGD sludge disposal to the land has been addressed. This effort considered the problem from a potential regulatory approach by evaluating the existing data base and projecting its potential impact on the promulgation of sludge disposal regulations. The Phase I portion of this effort has been published in a report entitled *Data Base for Standards/Regulations Development for Land Disposal of Flue Gas Cleaning Sludges*, EPA-600/7-77-118, December 1977.

The Phase II economic draft report (8) has been received and it is being processed into a final report publication to be entitled *Economic Impact Analysis of Alternative Flue Gas Desulfurization (FGD) Sludge Disposal Regulations on the Utility Industry.*

CONCLUSION

The laboratory and field research project efforts discussed here reflect the overall SHWRD effort in hazardous waste disposal research. The projects will be discussed in detail in the following papers. More information about a specific project or study can be obtained by contacting the project officer referenced in the text. Inquiries can also be directed to the Director, Solid and Hazardous Waste Research Division, Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, 26 West St. Clair Street, Cincinnati, Ohio 45268. Information will be provided with the understanding that it is from research in progress and that conclusions may change as techniques are improved and more complete data become available.

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ANALYSIS OF HAZARDOUS WASTES

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ABSTRACT

A paper on the characterization of hazardous waste would have never been included in such a symposium as this five years ago. However, since that time the impact of toxic and otherwise hazardous industrial waste products had become an important public and governmental concern.

The first major step toward solution of this problem was taken in late 1976 with the passage of Public Law 94-580, the Resource Conservation and Recovery Act (RCRA). This far reaching law, mandates the U.S. Environmental Protection Agency (EPA) to develop regulations for minimum standards for those who generate, transport and dispose of hazardous waste. In the words of Douglas Costle, EPA Administrator, "We do not underestimate the complexity and difficulty of our proposed regulations. Rather, they reflect the large amounts of hazardous wastes generated in our diverse society. The regulations will affect a large number of industry... as well as laboratories, pesticide applicators, and waste transporters. The agency estimates that approximately 270,000 waste generating facilities, 10,000 waste transporters, and many thousands of waste disposal and processing facilities will be regulated."

In the two years since the passage of RCRA, EPA has been working to develop these regulations, and on December 18, 1978, the core of the regulations was proposed in the Federal Register.

The phrase "core of the regulations" is used because the December 18th issue of the Federal Register covers what is called "Subtitle C" of RCRA. Subtitle C is directed toward the identification and characterization of hazardous wastes. The regulations in this section of the law outline biological and chemical testing methodologies by which these complex industrial and other toxic waste products may be examined to evaluate their potential hazard.

This highlights a key point in the regulation and management of hazardous waste. Such activities must be founded on an adequate understanding of waste composition. The generation of waste composition data by the laboratory is in many cases a formidable problem. However, if proper procedures are to be developed to assure safe handling, transportation, recycle, or disposal of waste, as well as assessment of public health and environment impacts, waste chemical composition must be known.

Our laboratory is attempting to develop a variety of methodologies to attach this problem. These include many of the modern instrumental techniques such as gas chromatography (GC), high pressure liquid chromatography (HPLC), atomic adsorpition spectrophotometry (AAS), X-ray fluorescence (XRF), and gas chromatography/mass spectrometry (GC/MS). In addition to these techniques, we have found that thin layer chromatography (TLC) is widely applicable to waste analysis, and has certain definite advantages over some of the more "equipment intensive" methods. Many laboratories which must provide data on waste composition do not have the financial resources to obtain expensive sophisticated instrumentation. TLC in these laboratories is an ideal alternative.

The approach taken by our laboratory has been one of a phased, or multilevel characterization. These phases are:

Phase I	Field Tests
Phase II	Laboratory Hazard Assessment Tests
Phase III	Laboratory Sample Preparation and Screening Tests
Phase IV	Laboratory Confirmatory Tests

An analytical scheme based on these four phases is currently under development. To date, the greatest emphasis has been placed on phases III and IV, and they will be the primary subject of this paper.

TEST PHASE I (FIELD TESTS)

This phase is intended for field assessment of the physical and chemical properties of the wastes. This includes the measurements of the properties of wastes that rapidly changes with time such as pH, and other properties that can cause injury to field personnel or immediate damage to public health and the environment such as generation of toxic gases, radioactivity, flammability, or explosivity. Other properties such as odor and color that may contribute to the preliminary characterization of the wastes are also noted. Table 1 lists the suggested field tests to be performed.

TABLE 1. SUGGESTED FIELD TESTS

Method	Applications & Limitations
Color test	Certain compounds and metallic ions have characteistic colors. These colors may serve as indicators of the predominant components in the waste. This method is very subjective.
Odor test	Odors of certain gases and other volatile substances are very distinctive. This information can assist in determining the group or classes of compounds in the wastes. This method is subjective. No instrument has yet been invented to measure odor.
Temperature test	Elevated temperature of a sample considerably above ambient indicates possibly exothermic reaction is taking place. Special precautions must be observed in handling the waste to avoid accidents. Temperature measurements are conveniently taken with a thermometer.
pH	A low pH is indicative of the presence of strong acids; high pH that of strong alkali. This information indicates that the waste is hazardous and must be treated as such. The information also alerts the analyst to test for strong acid and bases. pH is measured in the field with a pH paper or a portable pH meter.
Detector tubes	A number of detector tubes for gases are commercially available. These tubes provide quick tests for the presence or absence of most common toxic gases. One single tube can detect the presence of more than 20 gases. To identify a gas, a certain volume of the gas is aspirated through a detector tube specific for the gas. The concentration of the gas is proportional to the length of the color change in the tube. The waste is hazardous when a toxic gas is detected to be generated from it. Accuracy of most detector tubes range from 20 to 50%.
Radioactivity	Radiation from waste is measured with a radiation counter capable of detecting alpha, beta and gamma radiations. Portable Geiger counters are most useful. When a waste is found to contain radioactive material, the proper regulatory agency should be notified for immediate action.

TABLE 2. TEST PHASE II METHODS

Method	Applications
Bioassay test	Whole and/or separated phases of liquid waste mixtures are used for this test. The 96-hour LC_{50} of the waste must be determined on fathead minnows (pimephales promelas). If a waste dilution of 100 mg or less per liter of water kills on-half or more of the population of the test fish in 96 hours, the waste is hazardous.
Flash point	Whole and/or separated organic phase of liquid waste mixture is determined by ASTM D56-70, Standard of Test for Flash Point by Tag Closed Tests. Any liquid waste with a Flash Point of 100°F or less is flammable, thus hazardous.
Total acidity	This is a measure of the ability of the waste to neutralize a strong base. High acidity indicates the presence of strong mineral acids and/or hydrolyzable salts of mineral acids.
Total alkalinity	This is a measure of the ability of the waste to neutralize a strong acid. High alkalinity indicates the presence of mostly hydroxyl ions, and partly carbonate and bicarbonate ions.
Explosivity test	This test is used to determine whether the waste is sensitive to shock or detonates on impact. An explosivity meter or impact apparatus for explosivity can be used. Explosive wastes are hazardous.
Waste extraction test	This test is used to determine the leachability of the components of a solid waste. If the total soluble concentration of any component exceeds the soluble threshold limit concentration for that substance, the waste is hazardous.

TEST PHASE II (LABORATORY HAZARD ASSESSMENT TESTS)

The objective of this test phase is to confirm some of the field data and to obtain more information about the hazardous properties of the waste sample under controlled laboratory conditions. Tests included in this phase are bioassay, flash point, explosivity, total acidity, total alkalinity, waste extraction test and toxic gas generation. Small portions of the whole or phase separated sample is used for the test. Results from these tests, in some cases, is adequate to characterize a waste as nonhazardous, hazardous or extremely hazardous. Further analysis of the waste sample is continued when isolation and quantitation of the hazardous components are required. Table 2 outlines the suggested Test Phase II methods.

TEST PHASE III (LABORATORY SAMPLE PREPARATION AND SCREENING TESTS)

The initial step in this phase is the high speed centrifugation of the liquid waste mixture at 7,000 to 17,000 RPM to separate the aqueous, organic and solid phases. The separated phases are then subjected to qualitative compositional analysis using various procedures to obtain such information as the identify of organic functional groups and chemical classes, and that of certain suspected and more commonly

TABLE 3. TEST ON ORGANIC PHASE

Procedure	Purpose
Beilstein test	To detect presence of organic chlorides
Spot tests	To detect organic functional groups and simple compounds
Flash point	To determine flammability
Bioassay	To determine toxicity to organism
UV	To detect presence of aromatic and unsaturated compounds
IR	To determine molecular structures
TLC	To separate and preliminarily identify components
Column chromatography	To separate components according to molecular weight
Distillation up to 95°C	To collect low boiling distillates for identification
Residue at 550°C	To determine presence of organometals and metals

TABLE 4. TESTS FOR AQUEOUS PHASE

Procedure	Purpose
Residue at 550 C	To determine presence of metals and metallic compounds
Acidity	To determine presence of strong acids, and corrosivity
Alkalinity	To determine presence of strong alkali, and corrosivity
Beilstein test	To determine the presence of dissolved organochlorides
Spot tests	To determine functional groups of water soluble organic compounds, and simple organic and inorganic compounds
Redox potential	To determine presence of strong oxidizing or reducing agents
Anion analysis	To determine presence of anions such as $SO_4^{=}$, $N_O{}^-{}_3$, Cl^-, CN^-, etc.
TLC	To separate dissolved organic and certain inorganic compounds
Volatiles up to 95°C	To collect volatiles with boiling points up to 95°C
Extraction with solvent	To separate solvent soluble compounds from others

TABLE 5. TESTS FOR SOLIDS AND SOLID PHASE

Procedure	Purpose
TLC	See Table 4
Volatiles up to 95°C	See Table 4
Extraction with solvent	See Table 4
Residue at 550°C	See Table 4
Acidity	See Table 4
Alkalinity	See Table 4
Beilstein test	See Table 3
Spot tests	See Table 3
Redox potential	To determine the presence of strong oxidizing or reducing agent
Anion analysis	See Table 4
Organic solvent solution	To perform tests as for organic phase (Table 3) except the distillation test up to 95°C

occurring simple organic and inorganic compounds. Separation procedures such as thin layer and column chromatography or distillation are also used to isolate groups or individual components. TLC, particularly, is a simple, fast and inexpensive separation procedure that can be used when very little information about the waste is available. The isolated components are further examined with the compositional test procedures (i.e., U.V., I.R., Beilstein test) before Test Phase IV procedures are applied. In some cases, the separated phases of the sample are subjected back to the Test Phase II procedures for assessing whether the separated phases are more hazardous than the whole sample. Other times the separated phases are directly analyzed by the Test Phase IV procedures without performing any additional Test Phase II procedures. This usually happens when information is desired only on one or two suspected components of the waste sample.

A solid waste sample in this test phase is extracted with a solvent or solvent combinations by dissolution or by using a Soxhlet extractor. Aqueous and organic solvent solutions of the solid sample may also be prepared and subjected to the same test procedures as used for the separated aqueous and organic phases. The solid sample can also be subjected back to Test Phase II procedures for bioassay and waste extraction test and.or directly analyzed for metallic elements by AA, XRF or inductively-coupled plasma (ICP) atom analyzer in Test Phase IV.

After conducting Test Phase III procedures, usually enough information is known about the waste components. In some cases, some components are presumptively or close to being identified. When further characterization of the components are desired, the Test Phase III information serves as a guide in selecting the proper instrumental methods and optimal operating parameters that can be used in Test Phase IV. For instance, when low boiling chlorinated hydrocarbons are identified in a sample, one most certainly would select to use a GC with an electron capture detector. Test Phase III procedures prescribe the Test Phase IV procedures to be used. Tables 3, 4, and 5 show the different suggested procedures for Test Phase III.

TEST PHASE IV (LABORATORY CONFIRMATORY TESTS)

This phase of the analytical scheme consists of the state-of-the art instrumental analytical methods. These methods include atomic absorption (AA) spectrophotometry, gas chromatography (GC), gas chromatograph/mass spectrometry (GC/MS), high pressure liquid chromatography (HPLC), X-ray fluorescense spectrometry (XRF) and inductively-coupled plasma (ICP) atom analysis. These methods are expensive and complex requiring skilled and trained analysts to operate and maintain them as well as to interpret the data generated. Despite their high costs and sophistication, these methods are necessary in the analysis of complex mixtures such as hazardous wastes. The specialized methods can be used, in some instances, to analyze waste samples directly or with minimal sample pretreatment or preparation. In most cases, however, due to multiple inherent interferences, the waste samples are first subjected to clean-up, isolation, fractionation or partition procedures such as in Test Phase III. Components of wastes which have been presumptively identified in Test Phase III are definitively identified and quantitated with these methods.

ANALYTICAL APPROACHES

Different analytical pathway will be included in the analytical scheme to cover most types of wastes. A sample submitted to the laboratory for analysis is first visually examined. Its physical state, color and other characteristics are noted. These data in addition to field test results, if any, and the background information usually furnished by the sample collector, provide the basis for the analytical strategy. The analytical scheme will be consulted and the best possible analytical approach is selected. For example, the scheme provides the following analytical pathways for liquid/solid waste mixtures:

(1) Mixture - → AA or XRF or ICP

(2) Mixture - → Centrifuge at 7-17K RPM - organic, aqueous and solid phases

(3) Organic phase → flash point

(4) Organic phase → GC and/or HPLC; and/or GC/MS

(5) Organic phase → TLC → GC and/or HPLC; and/or GC/MS

(6) Organic phase → distill, 95°C → (4) and/or (5); and/or (7); and/or (8)

(7) Organic phase → TLC and/or Beilstein test; and/or spot test; and/or UV; and/or IR; and/or column chromatography GC and/or → GC/MS

(8) Organic phase → residue at 550°C → AA and/or XRF; and/or ICP

(9) Aqueous phase → acidity/alkalinity → Beilstein test; and/or spot test; and/or redox potential; and/or anions analysis; and/or volatiles; and/or organic solvent extraction

(10) Solid phase → pathways (11) to (15) (for solids) (not included nor discussed in this paper)

Analytical pathway (1) is chosen when analysis for metals is required. Instrumental methods such as the AA, XRF or ICP are used for the analysis. Wet chemical methods can also be used for analyzing the individual metals, but presently are seldom used because they are often time consuming and suffer from poor reproducibility. The AA is the least expensive of the three instruments, but metals can only be analyzed only one at a time. The XRF and ICP are very expensive, however, up to 60 metallic elements can be analyzed simultaneously.

Analytical pathway (2) is to separate the different phases of a mixed sample. A portion of the sample is centrifuged at 7,000 to 17,000 RPM. The separated phases are isolated and analyzed according to pathways (3) to (10).

The first analysis that might be performed on the organic phase is flash point. This is indicated in analytical pathway (3). Flash point is determined by the Tag Closed Cup procedure. When the flash point exceeds the hazardous flammability standard, further analysis of the sample may not be necessary.

When chemical analysis of the organic phase is required, any one or combinations of pathways (4) to (8) are used. In pathway (4) the sample may be injected directly into either a gas chromatograph (GC), high pressure liquid chromatograph (HPLC) or gas chromatograph/mass spectrometer (GC/MS) or any combination of the three. In most cases, the use of one of the three instruments is adequate to provide the analysis required. The GC is perhaps the first instrument of choice. It is fairly easy to use; a good analytical laboratory must have at least one GC. Volatile and heat-stable organic compounds can usually be analyzed by GC. The HPLC is a relatively new analytical tool and can be used to analyze practically most of the organic components of hazardous wastes. It can be used to analyze gas chromatographable substances as well as heat-degradable and high-boiling compounds.

Different sets of operating parameters for each of the instruments will provide resolution for different groups of compounds. The parameters to be used depend on the types of compounds suspected to be present in the sample. The choice of the parameters can usually be made by consulting the literature or the data from previous works. The parameters may be varied until optimal partitioning of components is obtained or all components of interest are resolved. If a sample, for example, is to be analyzed on an HPLC for thiosphosphate-type pesticides, the following analytical conditions may be used:

Column: Reversed phase, PXS-1025 ODS

Solvent System: 60/40 MeOH/H_2O at 1.6 ml/min.

Detector: UV at 254 nm

Temp: Room temperature

Again, the parameters may be altered until all components are identified.

Final confirmation of most organics is done by GC/MS. Often complex sample are very difficult to handle by any other method. The current expense of mass spectrometry equipment precludes its use by many laboratories.

In analytical pathway (5), thin layer chromatography (TLC) is first employed before instrumental analysis is attempted. In many cases, components of hazardous waste samples are separated by TLC. Different TLC systems as well as the application of different developing or chromogenic sprays on the separated components often indicate the presence of distinctive types of compounds. Comparison of the R_f values or the developed color of the TLC spots with that of standards often presumptively identify the compounds. The tentative identifications are further confirmed by either GC, HPLC or by GC/MS. The TLC information narrows down the selections, of the instrumental analytical parameters. For example, if by TLC systems a sample contains mostly chlorinated hydrocarbons, immediately the instrument of choice will be most likely the GC with electron capture detector. If high-boiling organics are indicated, confirmatory analysis can most likely be achieved by using the HPLC.

Preliminary analysis by TLC in most cases saves considerable analysis time and cost. It should be used for quick screening of the components of samples.

In analytical pathway (6), the distillate at 95°C is first collected. The distillate and/or the higher boiling fraction are analyzed by either or combinations of pathways (4), (5), (7) or (8). The distillation segregates the lower-boiling components thus enhances faster identification. The lower-boiling fraction may contain compounds with lower molecular weights as well as those responsible for flash points below 37.8°C.

In analytical pathway (7) several simple tests are first performed before the instrumental analysis. The preliminary test provide information such as the presence of functional groups or classes of compounds in the sample. Often times tentative identification of compounds is achieved by these tests. Table 3 outlines the information that results from these tests. The preliminary information obtained serves as the basis for selecting the analytical instrument and/or confirmatory operating parameters such as the examples given in (4) for further analysis of the sample.

Analytical pathway (8) requires ashing of the sample at 550°C. Appearance of a residue indicates the presence of organometal in the sample. The residue or sample is then analyzed by AAS, XRF or ICP for the metal(s).

The separated aqueous phase of the sample is analyzed using pathway (9). This pathway consists of several tests that may be performed. Combinations or all of the indicated tests might be necessary to analyze the sample. The measurement of pH is more accurately done with a pH meter. Acidity/alkalinity is determined by titrating a portion of the sample with standard base or acid to pH 3.7. High acidity/alkalinity values indicate the presence of strong base or acid. Positive Beilstein test usually indicates the presence of chlorinated hydrocarbons. Spot tests can show the presence of functional groups, classes of compounds and dissolved compounds. Redox potential can indicate the presence of highly ionized electrolytes. Anion analysis can identify negative ions such as sulfates, nitrates, cyanides and others. Water soluble organics can be separated from the aqueous phase by distillation, volatilization or by organic solvent extraction. Other phases are analyzed by different routes through the analytical scheme.

Analytical pathways intended for solids (11 to 15) and liquids (16 to 18) will also be included in the analytical scheme. These will not be discussed in this paper.

This report is part of a more complete work for the preparation of an analytical procedural manual for the analysis of hazardous wastes. The work has been supported by the U.S. Environmental Protection Agency, Municiapl Environmental Research Laboratory, Cincinnati Ohio, Richard A. Carnes, Project Officer.

HAZARDOUS WASTE COMPATIBILITY

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ABSTRACT

This report describes a method for determining the compatibility of the binary combinations of hazardous wastes. The method consists of two main parts, namely: 1) the stepwise compatibility analysis procedures, and 2) the hazardous wastes compatiblity chart. The key element in the use of the method is the compatibility chart. Wastes to be combined are first subjected through the stepwise compatibility procedures for identification and classification, and the chart is used to predict the compatibility of the wastes on mixing.

INTRODUCTION

The method of determining hazardous waste compatibility briefly described herein is an attempt to provide those in the waste management industry and the regulatory agencies with a systematic approach to reducing the risk to the public health and the environment of handling, processing, transporting and disposing hazardous wastes. Many service accidents have resulted from the mixing of incompatible hazardous wastes. These often violent chemical reactions have resulted in damage to public and private property, injury and sometimes death to individuals, and disposal of hazardous materials in the environment. These accidents most often occur because waste handlers have inadequate knowledge of the chemical compositions of the wastes, or are unaware of how chemical components of different waste types interact.

The objectives of the method are to:

1) Present the chemical reactions which are likely to produce signficant hazards to waste handlers and the environment.

2) Present a listing of chemical classes based on molecular structure and chemical reactivity which typically occur in wastes.

3) Provide guidelines for estimating which chemical classes occur in specific wastestreams.

4) Provide a method for estimating the potential consequences of mixing of different classes of wastes.

This paper very briefly describes the method which was presented to the U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory in the form of a manual or handbook (Hatayama, et al.) under a grant entitled, "Hazardous Waste Sampling, Analysis, and Compatibility Study." The contract officer for this work is Richard A. Carnes.

The manual should be considered an interim report on the study of hazardous waste interactions. Many shortcomings in the available data were revealed during the course of its development. These are currently being address by laboratory investigations. Development of a field method for testing hazardous waste compatibilities is also underway.

The best available knowledge of case histories of accidents, wastestream composition and chemical reaction consequences was used in developing this method. Department of Health Services files (California Department of Health Services[3]), U.S. EPA Hazardous Waste Disposal Damage Association (Manufacturing Chemists Association[7]), and other sources. Wastestream composition data was derived from the California Liquid Waste Hauler Record (California Department of Health Services[4]), U.S. Environmental Protection Agency's hazardous waste surveys (Assessment) of Industrial Hazardous Waste Practices.Chemical reactivity data was derived from textbooks, and sources dealing primarily with hazardous chemical interactions such as the Handbook of Reactive Chemical Hazards (Bretherick[2]), the Fire Protection Guide on Hazardous Materials (National Fire Protection Association[9]), Dangerous Properties of Industrial Materials (Sax[10]), and others.

HAZARDOUS WASTE COMPATIBILITY CRITERIA

Many types of hazardous wastes, are extemely reactive. In combination with other wastes or other materials, such wastes may react to cause very undesirable and uncontrollable consequences. These adverse consequences include: 1) heat generation (reaction code H). 2) fire (F), 3) innocuous gas N_2 or CO_2, such as generation which can cause pressurization (G), 4) toxic gas, such as HCN or H_2S, generation (GT), 5) flammable gas, such as H_2 or C_2H_2, generation (GF), 6) explosion due to extremely vigorous reactions or reactions producing enough heat to detonate unstable reactants or reaction products (E), 7) violent polymerization resulting in generation of extreme heat and sometimes toxic and flammable gases (P), 8) solubilization of toxic substances including metals (S). These consequences often cause injury and sometimes death to individuals in the area. They result in the disposal of extremely hazardous materials which threaten the environment and public health.

CAUSES OF ACCIDENTS

The full manual, "A Method for Determining Hazardous Waste Compatibility" (Hatayama, et al.[5]) documents twenty-four incidents involving adverse consequences from mixing of incomaptible hazardous wastes. This is not a complete list by any means but it provides a basis for the above mentioned compatibility criteria and for general observations relating to causes of such incidents. Three primary causes have been identified.

The first primary cause is the insufficiency or inaccuracy of information about the waste. Hazardous wastes are often complex mixtures of chemicals. In order to define them accurately, laboratory analysis is often required. This is expensive and frequently not performed. Waste generators often do not maintain adequate records of the components of their wastestreams. In some cases, information about certain wastestreams are deleted or altered to reduce the cost of disposal. In other instances, the properties of some waste change with time and temperature thereby producing more hazardous and unknown components. Persons handling the wastes often have insufficient or inaccurate information on which to base transportation and disposal decisions.

The second primary cause of accidents is indiscriminate handling of the wastes. Often supposedly "empty" containers actually contain hazardous residues which react adversely with the materials added. Haulers, uninformed of hazardous chemical interactions, often "top-off" their loads on the way to the disposal site (California Department of Health Services[3]). This often initiates chemical reactions in the tank truck which result in violent

HAZARDOUS WASTE COMPATIBILITY CHART

REACTIVITY GROUP NO.	REACTIVITY GROUP NAME													
1	Acids, Mineral, Non-oxidizing	1												
2	Acids, Mineral, Oxidizing		2											
3	Acids, Organic		G H	3										
4	Alcohols and Glycols	H	H F	H P	4									
5	Aldehydes	H P	H F	H P		5								
6	Amides	H	H GT				6							
7	Amines, Aliphatic and Aromatic	H	H GT	H		H		7						
8	Azo Compounds, Diazo Compounds, and Hydrazines	H G	H GT	H G	H G	H			8					
9	Carbamates	H G	H GT						G H	9				
10	Caustics	H	H	H		H				H G	10			
11	Cyanides	GT GF	GT GF	GT GF					G			11		
12	Dithiocarbamates	H GF F	H GF F	H GF GT		GF GT		U	H G				12	
13	Esters	H	H F						H G		H			13
14	Ethers	H	H F											
15	Fluorides, Inorganic	GT	GT	GT										
16	Hydrocarbons, Aromatic		H F											
17	Halogenated Organics	H GT	H F GT					H GT	H G		H GF	H		
18	Isocyanates	H G	H F GT	H G	H P			H P	H G		H P G	H G	U	
19	Ketones	H	H F						H G		H	H		
20	Mercaptans and Other Organic Sulfides	GT GF	H F GT						H G					
21	Metals, Alkali and Alkaline Earth, Elemental	GF H F	GF H F	GF H F	GF H F	GF H F	GF H	GF H	GF H	GF H	GF H	GF H	GF GT H	GF H
22	Metals, Other Elemental & Alloys as Powders, Vapors, or Sponges	GF H F	GF H F	GF					H E GT	U	GF H			
23	Metals, Other Elemental & Alloys as Sheets, Rods, Drops, Moldings, etc.	GF H F	GF H F						H F G					
24	Metals and Metal Compounds, Toxic	S	S	S			S	S			S			
25	Nitrides	GF H F	H F E	H GF	GF H E	GF H			U	H G	U	GF H	GF H	GF H
26	Nitriles	H GT GF	H F GT	H							U			
27	Nitro Compounds, Organic		H F GT			H					H E			
28	Hydrocarbons, Aliphatic, Unsaturated	H	H F			H								
29	Hydrocarbons, Aliphatic, Saturated		H F											
30	Peroxides and Hydroperoxides, Organic	H G	H E		H F	H G		H GT	H F E	H F GT		H E GT	H F GT	
31	Phenols and Cresols	H	H F						H G					
32	Organophosphates, Phosphothioates, Phosphodithioates	H GT	H GT						U		H E			
33	Sulfides, Inorganic	GT GF	HF GT	GT		H			E					
34	Epoxides	H P	H P	H P	H P	U		H P	H P		H P	H P	U	
101	Combustible and Flammable Materials, Miscellaneous	H G	H F GT											
102	Explosives	H E	H E	H E					H E		H E			H E
103	Polymerizable Compounds	P H	P H	P H					P H		P H	P H	U	
104	Oxidizing Agents, Strong	H GT		H GT	H F	H F	H F GT	H F GT	H E	H F GT		H E GT	H F GT	H F
105	Reducing Agents, Strong	H GF	H F GT	H GF	H GF F	GF H F	GF H	H GF	H G				H GT	H F
106	Water and Mixtures Containing Water	H	H						G					
107	Water Reactive Substances	← EXTREMELY REACTIVE!												
		1	2	3	4	5	6	7	8	9	10	11	12	13

HAZARDOUS WASTE COMPATIBILITY CHART (Continued)

Reactivity Code	Consequences
H	Heat generation
F	Fire
G	Innocuous and non-flammable gas generation
GT	Toxic gas generation
GF	Flammable gas generation
E	Explosion
P	Violent polymerization
S	Solubilization of toxic substances
U	May be hazardous but unknown

Example:

$H_{F_{GT}}$ Heat generation, fire, and toxic gas generation

14																											
	15																										
		16																									
			17																								
				18																							
					19																						
			H	H	H	20																					
			H_E	GF_H	GF_H	GF_H	21																				
			H_E	GF_H		H_{GF_F}		22																			
			H_F						23																		
										24																	
			GF_H	U	GF_H	GF_H	E				25																
							H_P			S	GF_H	26															
							H_{GF_E}				H_{GF_E}		27														
								H_E						28													
															29												
			H_E	H	E	$H_{F_{GT}}$	H_E	H_G		H_G	H_{GF_F}	$H_{P_{GT}}$		H_P		30											
				H_P			GF_H				GF_H					H	31										
							H									U		32									
				H												H_{GT}			33								
						H_P	H_P	H_P		H_P	H_P					H_P	H_P	U	H_P	34							
							H_{G_F}				H_{GF_F}					$H_{F_{GT}}$					101						
							H_E	H_E	H_E	E	E					H_E	H_E		H_E	H_E	H_E	102					
							P_H	P_H	P_H	P_H	P_H					P_H	P_H		P_H			H_E	103				
H_F		H_F	H_{GT}	$H_{F_{GT}}$	H_F	$H_{F_{GT}}$	H_{F_E}	H_{F_E}	H_F		H_{F_E}	$H_{F_{GT}}$	H_E	H_F	H_F	H_G	H_F	$H_{F_{GT}}$	$H_{F_{GT}}$	H_{F_G}	H_{F_G}	H_E	$H_{F_{GT}}$	104			
			H_E	GF_H	GF_H	GF_H						H_{GF}	H_E			H_E	GF_H	GT_{GF_H}		H	GF_H	H_E	$H_{P_{GF}}$	H_{F_E}	105		
				H_G			GF_H	GF_H		S	GF_H								GT_{GF}						GF_{GT}	106	
DO NOT MIX WITH ANY CHEMICAL OR WASTE MATERIAL! EXTREMELY REACTIVE! →																											107
14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	101	102	103	104	105	106	107

WORKSHEET FOR DETERMINATION OF HAZARDOUS WASTE COMPATIBILITY

Waste A ____

Waste B ____

Name ______________________ Date ______________

WASTE A	WASTE B Name Group No.								
Name	Group No.								

and disastrous consequences. Rough handling of waste containers have resulted in the rupture or leakage of highly reactive materials (California Department of Health Services[3]). Inadvertant mixing of materials known to be incompatible have resulted in numerous accidents. (Manufacturing Chemists Association.[7]) Inadequately designed chemical treatment processes for purposes of detoxification of or resource recovery from hazardous waste has resulted in uncontrolled reactions. (U.S. Encivronmental Protection Agency).

The third primary cause is indiscrim-disposal. Bulk wastes which were known to be incompatible with already ponded wastes have been indiscriminately disposed of to the ponds at disposal sites. Some wastes are incompatible with the composition of the disposal area such as concentrated nitric acid and refuse in a sanitary landfill or acid in an abandoned salt mine. Containerized wastes, irrespective of contents, often are co-disposed and hazardous reactions result when the containers rupture or leak due to corrosion. (California Department of Health Services[3]).

BASIS FOR THE METHOD

The principal assumption underlying the method is that waste interactions are due to the reactions produced by the pure chemicals in the wastes. Included in this assumption is the condition that the chemicals react at ambient temperature and pressure and that their reactivities are uninfluenced by concentration and synergistic and antagonistic effects. By this assumption, the compatibility of a combination of wastes can be predicted by the reactivities of the chemical constituents in the respective wastes.

Available data indicate that hazardous wastes are ill-defined, complex mixture generated by a great variety of sources. No two types of wastes appear to be identical. Even a single process appear to produce different types of wastes. Laboratory analyses of wastes are not easily obtainable and are often very cursory due to high costs and the complexity of analytical methods required. Characterization of the wastes by analysis of the processes and the materials used appear to give inaccurate descriptions of the resulting wastes. The data indicate that each waste is unique and their individual reactivities may be best assessed by identifying their respective chemical constituents. This information supports the pure chemical approach used in determining the reactivities of the wastes in the development of the compatibility method.

HAZARDOUS WASTE COMPATIBILITY CHART

The key to this method is the Hazardous Waste Compatibility Chart (Figure 1). It represents a two dimensional matrix of forty-one functionality, (Reactivity Group Number (RGN) 1 through RGN 34), and general chemical reactivities (RGN 101 through RGN 107). The more than one thousand compounds considered in the development of this method are classified into one or more of these reactivity groups.

The potential consequences of mixing compounds from one reactivity group with compounds from another are denoted by reaction codes in the square representing the combination of their RGN's. The reaction codes (RC) and consequences are detailed in a Table to the right of the matrix. These codes represent the Hazardous Waste Compatibility Criteria discussed earlier.

Many reaction squares contain multiple RC. These indicate that several consequences are predicted from the combination of two RGN. The order of the codes corresponds to the order in which the consequences are expected to occur. This is true for all multiple RC except for GTGF, where the gas that is produced is both toxic and flammable.

Many reaction squares contain the RC-U for "unknown". In these cases, the literature indicates that an adverse reaction between members of these RGN may occur. But, the consequences cannot be predicted at this time and actual experimental work may be necessary.

Blank reaction squares represent combinations which appear to be compatible. The literature indicates that adverse reaction consequences are not expected.

The number of RGN 107, "Water Reactive Substances" are considered to be extremely reactive that they should not be combined with any waste chemical or waste material. Although some neat chemicals are combined specifically with water reactive materials to preserve or protect them from decomposition, waste chemicals typically contain other constituents which may alter their protective chracteristics.

SUPPLEMENTS TO THE CHART

The chart is augmented by four appendices which are essential to determining the compatibilities of real wastes. The first is a list of chemical substances. This appendix lists are the compounds with appropriate synonyms which were considered in developing this manual in alphabetical order. It also lists in an adjacent column, the reactivity groups assigned to each compound. This appendix is used to determine the RGN(s) of a known chemical constituent of a waste.

The second appendix is a list of Waste Constituents by Chemical Class and Reactivity. It categorizes the compounds in the List of Chemical Substances into reactivity groups based on chemical functionality such as alcohols or carbamates, and on general chemical reactivity such as strong oxidizing agents and strong reducing agents. These reactivity groups correspond to those on the chart. This appendix is used to obtain the RGN(s) of a hazardous waste when its chemical constituents are known by chemical classes, molecular functionality or chemical reactivities. An example is if a waste is identified as containing alcohols, ketones, and water.

The third appendix is an Industry Index and List of Generic Names of Wastestreams. The Industry Index list names of industries in general terms alphabetically with their corresponding Standard Industrial Classification (SIC)(Standard Industrial Classification Manual) code numbers. This index is used to determine the general industrial class of a waste generator. The SIC code number obtained then allows entry to the List of Generic Names of Wastestreams which contains the names of typical wastestreams generated by industry. Such names include Citrus Pectin Wastes, Chromate Printing Wastes, Acetylene Manufacturing Sludges, etc. Each waste is assigned RGN(s) based on hazardous chemical constituents known or expected to be present in the wastes. This appendix is used to determine the RGN of Wastestreams when their compositions are not known specifically but are identified by their generic or common names.

The fourth appendix is a List of Incompatible Binary Combinations of Hazardous Waste Reactivity Groups and the Potential Adverse Reaction Consequences. This appendix describes in detail the potential adverse reaction consequences predicted in the Hazardous Waste Compatibility Chart. It is written for the hazardous waste manager who is well versed in reaction chemistry and can be used to make a more refined assessment of the compatibility of two waste types.

GENERAL PROCEDURES FOR DETERMINING HAZARDOUS WASTE COMPATIBILITY

The basic requirement for using this method is to classify the chemical components of a waste into one or more of the forty-one reactivity groups. Each RGN of one waste is then matched with each RGN of another waste to determine this compatibility. There are five general steps in the procedure:

Step 1 Obtain as much information as possible about the history and composition of the wastes. Such in many aspects of the management of hazardous wastes. It will be useful to the waste generators in identifying and segregating their wastes for disposal; to the transporters for segregating, combining, and/or proper containerizing of the wastes; to the site operators for determining co-burial of containerized wastes in the same cell or co-ponding of bulk wastes; to the regulatory agencies for determining suitability of sites for disposal of certain wastes; and to those who perform chemical treatment of the wastes for purposes of detoxification or resource recovery to present possible uncontrolled reactions.

This method cannot be used to predict all the potential incompatible reactions of any two given wastes, and neither can it furnish information on all hazardous wastestreams due to the tremendous variety of waste types, constituents, and characteristics. Additionally, the method does not address ternary combinations of incompatible hazardous wastes.

SUMMARY AND CONCLUSIONS

An extensive review of the literature and surveys of hazardous wastes management practices has shown that adverse reactions can result from the mixing or combination of incompatible hazardous wastes. These reactions have been categorized into twelve classes on the basis of reaction products with the potential of causing public health and environmental damage. The twelve classes are: 1) heat generation, 2) fire, 3) gas formation, 4) formation of toxic fumes, 5) generation of flammable gases, 6) volatilization of toxic or flammable substances, 7) formation of substances of greater toxicity, 8) production of shock and friction sensitive compounds, 9) pressurization in closed vessels, 10) solubilization of toxic substances, 11) dispersal of toxic dusts, mists and particles, and 12) violet polymerization.

Three primary causes of the combination of incompatible wastes were identified, namely:

1) insufficiency or inaccuracy of information about the wastes
2) indiscriminate handling of the wastes, and
3) indiscriminate waste disposal practices.

In order to present and/or minimize the chances of combining incompatible hazardous wastes and to avoid the resulting adverse reactions, it was determined that a method of determining wastes compatibility is necessary. Such a method was developed for the binary combinations of wastes types. A compatibility method addressing ternary or more combinations was considered, but found to be unwieldy. In the binary method the potential for occurrence of any one of the twelve identified reactions was taken as an indication of incompatibility. The determination of the occurrence of incompatible reactions was based on the assumption that the waste reactions are results of pure chemical components of the wastes reacting at ambient temperature and pressure. These assumptions are made primarily for reasons of simplification, however, it is believed that they are justified in view of most disposal and transport situations.

The development of the stepwise procedures for the compatibility method required the assignment of waste components into reactivity groups based on molecular functionality and reactivity characteristics. Using this procedure, it was found that the reactivity group(s) of the components of one waste paired with the reactivity groups of another waste could predict the potential occurrence of certain incompatible reactions. A two dimensional graphic display was determined as the best method for presenting the reactivity groups and allowing for intergroup pairing. This resulted in the development of the compatibility chart presented in Figure 1. Color coding of group pairings can be included to aid in rapid determination of potential incompatibilities.

A primary conclusion which was reached from this work was that there is a dearth information can usually be obtained from records of the waste producers, the manifests that accompany the wastes and examination of the processes that produced the wastes. When no information is available, collect representative samples of the wastes and submit them for analysis. The analysis shoud provide information on the specific chemical constituents or classes of compounds in the wastes.

Step 2 Starting with one waste, Waste A, List the names of or the classes of compounds found in the waste, or list its generic name on the vertical axis the Worksheet for Determination of Hazardous Waste Compatibility (Figure 2). The composition of a waste is Known Specifically when the constituents are listed by chemical names such as ethylene glycol, sodium nitrate, etc. The composition is Known Nonspecifically by Classes when the constituents are identified only by chemical classes or reactivities such as alcohols, caustics, mercaptans, etc. The composition is Known Nonspecifically by Generic Name when the waste is classified as spent caustic, tanning sludge, copper plating waste, etc.

Step 3 When the composition of Waste A is Known Specifically by chemical names, consult the List of Chemical Names to obtain the RGN's for each chemical constituent. These RGN are then noted on the Worksheet. If a compound is not on the list, a synonym can be found in various chemical references (Merck[8], Hawley[6]). When a suitable synonym cannot be found, the RGN of the component may alternatively be determined based on its chemical class or reactivity.

When the composition of the waste is Known Nonspecifically by Classes, consult the List of Waste Constituents by Chemical Class and Reactivity to determine the corresponding RGN.

When the composition of the waste is Known Nonspecifically by Generic Name, go to the Industry Index and List of Generic Names of Wastes to obtain the corresponding RGN are noted on the worksheet.

Step 4 Repeat Steps 2 and 3 for the second waste, Waste B, and note the information on the horizontal axis of the Worksheet.

Step 5 Consult the Hazardous Waste Compatibility Chart (Figure 1) and note the Reaction Codes (RC) between all binary combinations of RGN of Waste A and Waste B. If any RC corresponds to any binary combination of RGN between Wastes A and B, then Wastes A and B are incompatible and should not be mixed. Details of the potential adverse reactions can be obtained from the List of Incompatible Binary Combinations of Hazardous Wastes Reactivity Groups and the Potential Adverse Consequence.

SCOPE, APPLICATION AND LIMITATIONS OF THE METHOD

The method provides a systematic approach for determining the compatibility of most binary combinations of hazardous wastes produced by industry and agriculture. The method also provides a list of compounds known or expected to be present in hazardous wastes. Lastly, the report classifies the compounds as well as the wastes into chemical reactivity groupings and lists the potential adverse reaction consequences of most incompatible binary combinations of the groupings.

This method will be useful reference

of information about the reactivities of chemicals in the complex matricies of wastes. Many factors assuredly do greatly influence waste component reactions. Among these are temperature, catalytic effects of dissolved or particulate metals, soil reactions and reactions with surfaces of transport vehicles or containers. The simplified compatibility methodology which has been developed in this study, however, should provide a useful aid to persons involved in generating, transporting, processing, and disposing of hazardous wastes if reasonable precaution is taken in its use.

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MONITORING WELL SAMPLING AND PRESERVATION TECHNIQUES

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ABSTRACT

Water sample collection and preservation techniques have been established by several laboratories and agencies to insure that water samples received are chemically representative of water contained in the aquifer being monitored. However, there is considerable controversy between laboratories, agency policies, and researchers concerning the proper sampling techniques from monitoring wells and the appropriate preservation procedures of the samples for various chemical constituents. The development of recommended sampling procedures and preservation techniques for certain types of wells and specific chemical constituents is the principal goal of this study. Samples have been collected from six study sites using four different pumping mechanisms and various sample preservation techniques. This paper describes the experimental procedures being used and presents preliminary results based on work to date. Data collected thus far demonstrate that the length of pumping (time), type of pumping mechanism used, and size of membranes used to filter the samples all affect the chemical composition of water collected from monitoring wells.

INTRODUCTION

Regulatory agencies are charged with the assignment of regulating the disposal of waste to insure that the environment is not adversely affected. To accomplish this task, it is necessary for these agencies to set design and operational standards based on available technology to minimize potential pollution. The operating disposal facilities must then comply with these standards. They also must monitor the effects of their operation on the surrounding environment. The use of wells or piezometers for collecting water samples and water level data has been, and probably will continue to be, the traditional method for monitoring the effects of waste disposal facilities on groundwater.

Much research has been conducted to develop analytical laboratory techniques to detect the low levels of various constituents set forth in water quality standards. Water sample collection and preservation techniques have been established by several different laboratories and agencies in an attempt to insure that water samples delivered to the laboratory are chemically representative of water contained in the aquifer being monitored. However, there is considerable controversy between laboratories, agency policies, and researchers concerning proper techniques of sampling from monitoring wells and the appropriate procedures for preserving the samples for various chemical constituents. If monitoring wells and water samples are to provide the performance yardstick of disposal facilities design and operation, the question of significance of the various sampling procedures and preservation techniques should be determined.

This report is the result of work performed on a project partially funded by the U.S. Environmental Protection Agency, Cincinnati, Ohio, Grant No. R-806304-01-0. This report should be considered preliminary and subject to reinterpretation.

Purpose

The three principal purposes of this study are: 1) to determine if current sampling methods produce samples that are representative of water contained in the aquifer being monitored; 2) to determine if groundwater samples collected in the field must be treated (filtered and acidified) on location, or if they can be brought back to the laboratory for treatment without altering their chemical nature; and 3) to determine which sampling and preservation techniques should be accepted as standards for monitoring well sampling.

Specific Objectives

1. Determine the hydrologic properties of the materials tapped by each monitoring well studied.
2. Determine a pumping scheme for each well to obtain water samples representative of aquifer water.
3. Collect a series of samples from each well using four different pumping methods and various preservation techniques.
4. Determine the effects of time of pumping, pumping rate, pumping mechanism, and preservation techniques on the chemical results of samples collected.
5. Recommend sampling procedures and preservation techniques for monitoring wells for specific chemical constituents.

SITE SELECTION

Monitoring wells at six sites have been selected for study. These sites represent a cross section of hydrologic conditions and chemical characteristics of aquifer water. Two sites are active landfills; two are inactive landfills; one is a secondary zinc smelter; and one is a hog processing plant. The wells at all sites were in existence prior to this study and all but one was constructed by persons other than the authors. Five are cased with PVC pipe either 3.81- or 5.08-centimeters (1½- or 2-inches) in diameter. The sixth well is cased with 5.08-centimeter (2-inch) diameter galvanized iron. The well depths range from about 5 to 10 meters (16 to 30 feet) and have non-pumping water levels from 0 to 5 meters (0 to 16 feet) below land surface.

Factors considered in selecting the sites included: 1) accessibility to the monitoring wells so that pumping tests and sampling could be accomplished without undue hardship; 2) the physical characteristics of the monitoring well and geology of the location; 3) the potential yield capability of the materials tapped by the monitoring well; and 4) the chemical quality of water obtained from the monitoring wells.

PUMPING EQUIPMENT AND TESTS

Pumping Methods and Equipment

Four methods of obtaining samples from the monitoring wells are being used. These include samples collected by mechanical pumping means, an air-lift system, a nitrogen-lift system, and bailing. Most monitoring wells examined to date were 1½-inch or 2-inch diameter PVC wells. The small diameters create rather severe limitations on the selections of pumping apparatus.

The mechanical pump used was a Masterflex 7545 variable speed drive unit equipped with a model 7015 peristaltic pump head. When operated on 115 volts (a portable generator is used in the field), it is capable of producing from about 50 to 1000 milliliters per minute (0.013 to 0.264 gallons per minute).

For air-lift and nitrogen-lift pumping systems an apparatus similar to that shown in Figure 1 was used. For some sampling runs, a 1.27-cm (½-inch) diameter rigid PVC discharge pipe and 0.635-cm (¼-inch) plastic airline were used. For others a 0.952-cm (3/8-inch) diameter flexible polyvinyl discharge line and 0.635-cm (¼-inch) plastic airline were used. For all air-lift pumping a four-cylindar electric-driven air compressor was used.

For the nitrogen-lift pumping runs, 8.5 cubic meter (300 cubic foot) cylindars of nitrogen were used. A pressure regulator and Matheson type flowmeter were used

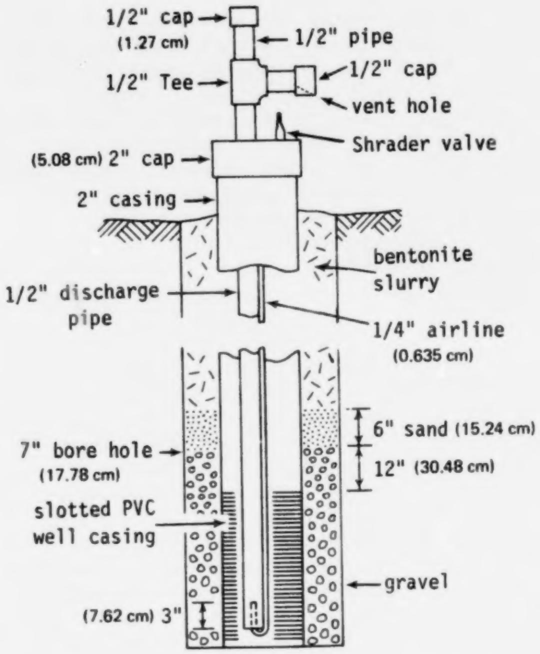

Figure 1. Typical Well and Air-lift Pumping Mechanism

to control the pressure and flow rate to the gasline.

Experience gained during the first year of the project concerning air-lift and nitrogen-lift pumping has demonstrated the need for more detailed experimentation with this type of pumping system. Laboratory data will be collected during the next year to more accurately define 1) the flow rates possible with varying discharge pipe size, 2) the amount of air or nitrogen required for given physical settings and desired water discharge rates, and 3) the limitations of this type of pumping mechanism.

A 2.54-cm (1-inch) diameter stainless steel bailer, 0.914-meters (36-inches) long was constructed to bail the test wells. This bailer retrieves a sample of about 350 milliliters.

Pump Test Results

Three pumping tests have been successfully completed to date. Discussion in this paper will be limited to the results of the pumping test at Site 1.

Site 1--Well No. 12 at the Sandoval Zinc Company site is a 5.08-cm (2-inch) diameter well 4.25 m (14.0 feet) deep. The well is cased with PVC pipe and has slots sawed in the bottom 60.96 cm (2 feet). The casing extends 54.87 cm (1.8 feet) above land surface.

A pumping test was conducted on this well on January 16, 1979. The well was pumped with a Jabsco self-priming pump at rates varying from 1750 to 1000 ml/min (0.462 to 0.264 gpm) for a period of 15 minutes before the pump broke suction. Water level recovery data were collected for a period of 30 minutes after pumping stopped. Discharge measurements were made with use of a graduated cylinder and stop watch. Water level measurements were made with a steel tape.

Two different approaches have been taken in analyzing all pump test data. First, the techniques developed by Papadopulos and Cooper[2] were applied to determine an aquifer transmissivity. In the case of the Sandoval test, the adjusted recovery data were used to determine an aquifer transmissivity of about 3600 m^2/day (200 gpd/ft). The aquifer transmissivity is used to compare the relative water yielding character of each site.

The second approach used in analyzing the pump test data is much more simplistic and problem oriented. Adjusted recovery data were examined at the end of each time increment during the recovery portion of the test to determine the rate of water delivered to the casing. This rate was then related to the average drawdown over the time increment of interest. Regression analysis relating aquifer yield (Q_a) to total water level drawdown (Tdd) for the Sandoval pump test data yielded the relationship Q_a=109.7+110.7 (Tdd). This relationship can be used to simulate total drawdown in the Sandoval well for different pumping rates.

In addition to being able to develop theoretical drawdown curves from this relationship, the amount of water coming from the aquifer can be calculated for each time increment. These amounts, represented as percentages of total (Q_t) pumpage $[(Q_a/Q_t) \times 100]$, are presented in Figure 2 for pumping rates of 2000, 1000, and 200 ml/min (0.528, 0.264, and 0.005 gpm). Based on these calculations for the Sandoval well, it appears that a pumping rate of 200 ml/min should produce water samples containing a higher percentage of aquifer water in the

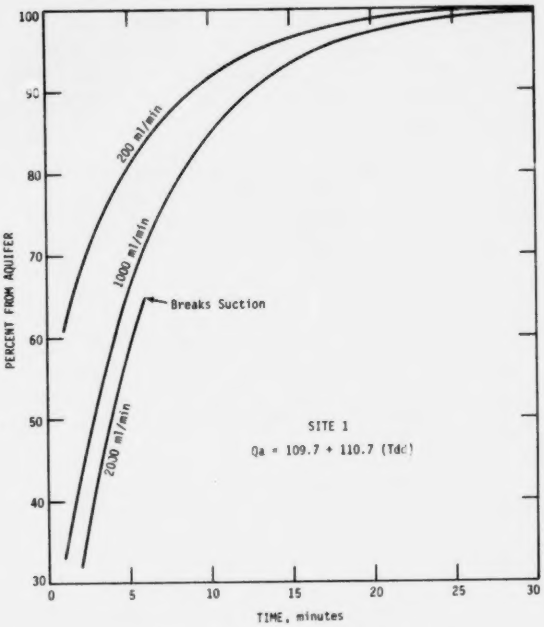

Figure 2. Site 1: Aquifer Yield Curves

shortest period of time. This statement is based on the assumption that the pump intake is located in the screened portion of the well near the bottom so that minimal mixing of aquifer and stored water from the casing will occur.

SAMPLE COLLECTION AND ANALYSIS

The techniques employed in the storage and preservation of water samples collected for environmental assessment will directly affect the chemistry of those samples. Many investigators have studied the effects of storage and preservation of aqueous samples. Rattonetti[3] studied the effects of preservation on surface waters and concluded that filtration and subsequent acidification were needed to maintain sample integrity. Subramanian et al.[7] looked at the storage of both synthetic and natural water samples held in several different types of containers at various pH's over periods of time. Their study concluded that acidification to a pH <1.5 and storage in linear polyethylene containers were most effective in avoiding the loss of metals from solution. Struepler,[6] Smith,[5] and Shendrikar et al.[4] are among the many investigators who have studied the adsorption characteristics of trace metals on the surfaces of various types of container walls.

These studies all were conducted with either natural surface waters or synthetic water samples whose constituent concentrations were in the mg/l range. Samples collected in this study, however, were taken from monitoring wells at industrial or municipal refuse sites where the constituent concentrations were considerably greater. In addition, these groundwater samples were being held under anaerobic conditions. This created additional preservation problems that may not be encountered with surface waters.

Another sampling decision was that of which pore sizes of filter membranes should be used. The use of 0.45 µm pore size cellulose acetate membranes has been widely accepted as the standard for sample preparation. However, in the case of water samples with high turbidity, the 0.45 µm membrane may be impractical for on-site filtration because of the slow filtration rate. A larger pore-sized membrane may be more applicable for these samples, but may also allow for the passage of clay-sized materials through the membrane. Acidification of these samples could result in the solubilization of particulate matter or leaching of trace metals from the clays which would produce high constituent concentrations that are nonrepresentative. Kennedy et al.[1] also showed that certain clay sized particulate material can pass through a 0.45 µm membrane.

While pumping at each site, samples were taken from the initial water in storage and at ½, 1, 1½, 2, 4, 6, 8, and 10 well volume intervals. Aliquots for analysis were taken from each of the well volumes or partial well volume samples collected. While on site, pH, Eh (oxidation-reduction potential), specific conductance, and alkalinity measurements were made on the unfiltered samples immediately after they were collected. The aliquots were then subdivided into three portions and filtered through either a 3.0 µm, 0.45 µm, or a 0.22 µm pore sized Millipore® membrane using Satorius® plastic filter holders. [Mention of trade names should not be considered as an implied or direct endorsement of the products mentioned. They are given for the convenience of the reader and do not indicate preferential treatment by the Illinois State Water or Geological Surveys.] Nitrogen was used as a pressure source to speed filtration and avoid degassing of the sample as may occur if a vacuum is applied. Each filtered subsample was then further subdivided into samples for analysis of cations and anions. The samples for cation analysis were preserved immediately after being filtered by addition of concentrated nitric acid to a pH <1.5. The samples for anion and nitrogen analysis were stored in an ice chest in the field and later at $4^{\circ}C$ in the laboratory. At Site 5 additional sample volumes were filtered through the 0.45 µm membrane for total organic carbon (TOC), nitrate and ammonia analysis. All of these samples were stored in linear polyethylene bottles. Samples for TOC analyses were preserved by addition of sulfuric acid.

The Jarrell-Ash Atom Comp 750 inductively coupled plasma unit was employed for sample analysis of Al, As, B, Ca, Cd, Cr, Fe, Mg, Mn, Pb, Se, and Zn. Sodium and K were determined by atomic adsorption. Chloride, fluoride, pH, and Eh were analyzed by ion selective electrode and sulfate was determined colorimetrically.

CHEMICAL RESULTS

Approximately 3500 samples and over 42,000 chemical analyses have been collected and analyzed to date. The data from these analyses are being evaluated in an effort to explain the variations in chemical concentrations with pumping or time, different pumping rates, pumping mechanisms, and different filter pore sizes. Additional data also are being collected to determine the effects of storage on sample integrity.

For this paper discussion will be limited to the effects of time of pumping, pumping rates, pumping mechanisms, and filter pore size on the chemical results of the collected samples.

Probably the single most important factor affecting the chemistry of groundwater is pH. Therefore, anything that alters the pH of the groundwater samples may alter the chemistry of its constituents. During sampling, extreme care was taken to obtain the most reliable pH measurements possible.

On-site pH measurements at all six sites using the four pumping mechanisms have been analyzed. The results illustrate two possible effects of the type of pumping mechanism on sample character. For comparison, all pH data for each site were normalized to the "stabilized" pH values obtained for 6-, 8-, and 10-well volume samples collected by the mechanical pump at that site. The "normalized" pH values therefore represent the relative differences in pH between mechanical pumping and the other pumping mechanisms. This was done to give a standard basis of comparison for all six sites. These normalized pH values are plotted in Figure 3 for each sample collected.

Data from samples collected by mechanical pump at all six sites are grouped along a normalized pH value of 100. The fluctuation in pH during the early stages of pumping (0 through 4 volumes) probably was due to the mixture of water stored in the well casing and aquifer water pumped into the well during this portion of sampling. As a higher percentage of aquifer water is pumped (volumes 6 through 10) the pH values begin to stabilize. The pH values converge and are thought to reflect the "true" pH of water in the aquifer.

Two other distinct groupings of data also are shown in Figure 3. During the pumping of samples by air-lift and nitrogen-lift, two different discharge pipe sizes were used, a 1.27-cm (½-inch) and 0.952-cm (3/8-inch). Data obtained from samples collected by either air or nitrogen, with 0.952-cm (3/8-inch) discharge pipe, appear to stabilize at a normalized pH value of

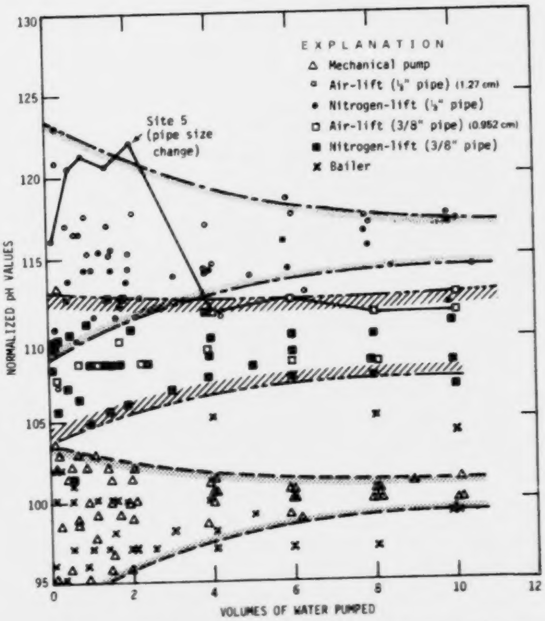

Figure 3. Effects of Pumping Mechanisms on pH Values

110. Data obtained from samples collected using either air or nitrogen with the 1.27-cm (½-inch) discharge pipe appear to stabilize at a normalized pH value of 116. In both groupings, larger fluctuations in pH values during the early stages of pumping were noted because of the mixing of stored and aquifer water, as with the mechanically pumped samples.

However, marked pH value changes were noted throughout the duration of sampling. It is postulated that the bubbling air or nitrogen passing through the water is stripping dissolved CO_2 that was in excess of atmospheric pressure from the water. This results in increased pH values over those obtained by peristaltic pump. Smaller changes were noted in the samples collected using the 0.952-cm (3/8-inch) discharge pipe. This was thought to occur because less air or nitrogen is needed to pump the same quantity of water than with the 1.27-cm (½-inch) discharge pipe. The gas to water ratios for the samples collected using the 0.952-cm (3/8-inch) diameter pipe varied from about 3.4 to 9.5, with the higher ratios generally resulting in larger pH changes. The gas to water ratios for the samples collected using the 1.27-cm (½-inch) diameter pipe were much higher (30.0 to 40.0) and appear to have effectively stripped the samples of most of their excess dissolved CO_2, resulting in pH values of 8.2 to 8.3. This can be compared with pH values of 6.9 to 7.0 when the peristaltic pump was used to collect samples.

Data from samples collected at Site 5 using an air-lift pumping mechanism dramatically illustrate the effect of pipe size on pH as shown in Figure 3. During the first stage of pumping (volumes 0 through 2), a 1.27-cm (½-inch) discharge pipe was used. To increase the pumping rate, the 1.27-cm (½-inch) pipe was withdrawn and a 0.952-cm (3/8-inch) pipe inserted between volumes 2 and 4. The immediate large drop in pH shown in figure 3 confirms the important effect of the gas to water ratios on the chemistry of water samples collected with these types of devices.

Results of pH measurements at the six study sites suggest that air-lift or nitrogen-lift pumping mechanisms do alter the chemistry of the collected sample. These effects could be minimized by proper design and operation of the pumping device for collecting water samples in certain physical settings (depths, water levels, and pumping lifts). However, since the changes in pH are significant in terms of some chemical constituents, these types of pumping mechanisms may not be desirable for collecting water samples in many cases. The metals (Fe, Zn, Cu, Pb, and Cd) appear to be particularly affected by the use of these pumping mechanisms, as any changes in pH are likely to affect the concentrations of metals in solution. The alkaline earth materials on the other hand appear to be somewhat insensitive to the effects of pH change induced by the different pumping mechanisms employed.

Figure 4 illustrates the change in iron concentrations with volumes of water pumped (time) at Site 5 for all four pumping mechanisms. The differences in iron content noted between samples collected mechanically and by nitrogen-lift principally are the result of pH change. The increased pH values of the samples collected by the nitrogen-lift mechanism probably is causing some soluable iron compounds to precipitate and fall out in the well casing or be filtered from the collected samples. More extreme effects are noted for samples collected by air.

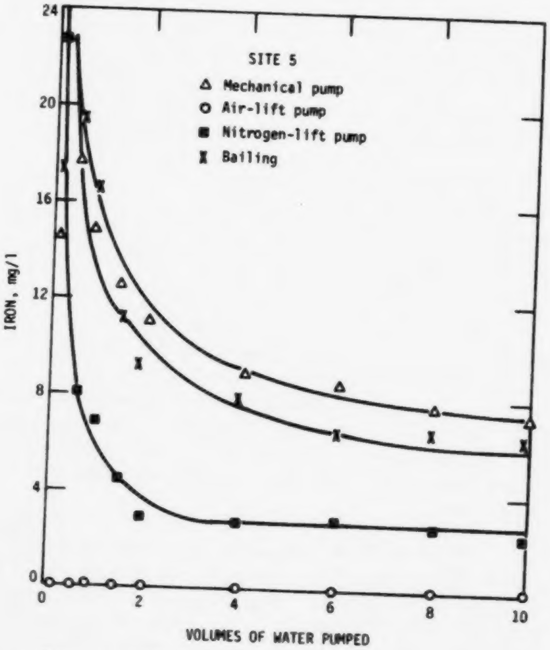

Figure 4. Effects of Pumping Mechanisms on Iron Concentrations at Site 5 as a Function of Well Volumes Pumped

Additional soluable iron was apparently oxidized and similarly removed, thus resulting in even lower iron concentrations than found in samples collected with nitrogen. The small differences in iron concentrations of samples collected mechanically and by bailing may be the result of seasonal fluctuations in iron concentrations.

Similar trends also were noted for other metals (Zn, Cu, Pb, and Cd). The effects on iron were more dramatic at the sites studied because of the relatively high concentrations and the anaerobic nature of landfill leachates and the anaerobic digestion ponds at the hog processing plant (Site 5).

Comparison of chemical analyses for the samples filtered through the three pore sizes of membranes indicated that, for certain constituents, the concentration was dependent upon the pore size employed. Figure 5 illustrates the effect of filter pore size on iron content of samples collected at Site 6 using the nitrogen-lift pumping mechanism. In all cases the higher iron concentrations were found in those samples filtered through the 3.0 µm pore size filters. The concentrations of the samples filtered through the 0.45 µm and 0.22 µm membranes were comparable to each other. However, there was a trend toward slightly lower values for samples filtered through the 0.22 µm membranes. This trend would indicate that some fine-sized material was passing through the 0.45 µm membrane. In comparing the concentrations of other metals (Zn, Cd, Cu, Mn, and Pb) there also was a trend towards decreasing concentrations with decreasing pore size. However, the concentrations of these metals are near the detection limit of the analytical procedures employed, making positive conclusions difficult.

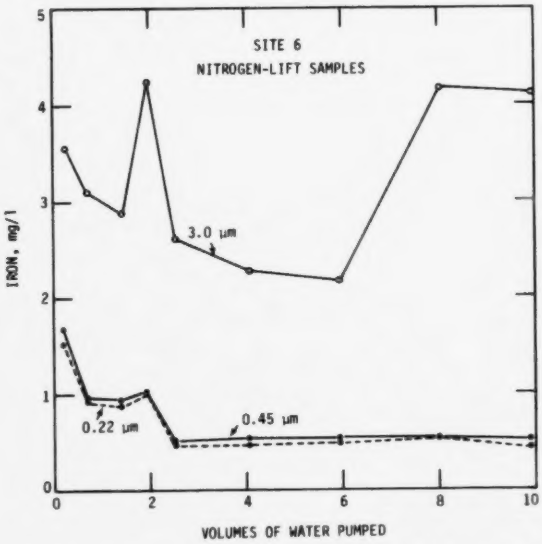

Figure 5. Effects of Filter Pore Size on Iron Concentrations of Samples Collected at Site 6 using a Nitrogen-lift Pumping Mechanism

Because of the complexity of the environmental systems being studied, it is difficult to determine the exact cause of the filtration effect. It is possible that the increased concentrations in the filtrates were due to the passage of fine clay particles, or possibly due to the passage of precipitates that formed prior to filtration and were later dissolved when the samples were acidified for storage.

SUMMARY

Data gathered during the first year of this project has demonstrated that the length of pumping, type of pumping mechanism used, and the size of membranes used to filter samples all affect the chemical composition of water collected from monitoring wells. The relative magnitude of their effects appears to be site specific and related to: 1) the yield potential of the sampled well; 2) the depth, diameter, and water level of the monitoring well; 3) the rate at which the well is pumped; 4) the general chemical character of the water being sampled; and 5) the specific elements that are to be monitored or analyzed.

During the next year of the project an attempt will be made to quantify as many of these variables as possible. Additional sampling and analyses will be undertaken to determine the effects of storing samples for various periods of time before they are filtered and analyzed. Additional sampling runs also may be undertaken to test hypotheses developed during the analyses of data collected to date.

Recommendations relative to specific sampling procedures and preservation techniques for certain types of wells for specific chemical constituents also will be made in the future.

ACKNOWLEDGMENTS

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THE UTILITY OF EXTRACTION PROCEDURES AND TOXICITY TESTING WITH SOLID WASTES

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ABSTRACT

Solid wastes from diverse origins were extracted using the proposed EPA extraction procedure (EP). These extracts were characterized chemically and tested for toxicity using bioassays for aquatic, phytotoxic, and mutagenic characteristics. None of the EP extracts appeared to be mutagenic, however, the negative responses may be due to the inability of the acidic, aqueous EP to extract nonpolar organics and/or possible sorption of these compounds on the type of filter used in the EP. Several of the extracts were toxic in the phytotoxicity and/or aquatic test systems. Acetic acid in the EP interfered in the phytotoxicity and aquatic toxicity bioassays, making interpretation difficult.

INTRODUCTION

To describe the potential environmental hazards of a solid waste, under Subtitle C of the Resource Conservation and Recovery (RCRA) of 1976 (PL 94-580), an extraction procedure (EP) was proposed by EPA in the December 18, 1978, Federal Register (43 FR 58956). The EP was established as an integral part of a screening protocol for the characterization of solid wastes as 'toxic' or 'nontoxic'. Concentrations of eight elements in the extract (10 times the EPA Primary Drinking Water Standard of As, Ba, Cd, Cr, Pb, Hg, Se, and Ag) are a primary basis for classification. Ideally, the protocol should be applicable to a diverse spectrum of wastes covering a wide range in physical and chemical characteristics. It should estimate the quantity of potential contaminants released as a function of time and disposal conditions. To be widely accepted, it should be relatively simple, rapid, inexpensive, and easily interpreted.

To assist the EPA in developing these protocols for identifying solid wastes that may pose a potential hazard to human health and environment, the Oak Ridge National Laboratory (ORNL) has conducted studies on the EP extract from seventeen solid wastes of diverse origin. Using these extracts, analytical procedures have been developed to chemically characterize and separate the organic and inorganic constituents in the waste. The EP extracts have been used in bioassays developed to test possible toxicity to aquatic organisms and plants. A battery of three bioassays diagnostic for detecting changes in genetic activity were used to serve as an indicator of chronic hazards relative to possible mutagenic and carcinogenic effects of the EP extract.

The purpose of this manuscript is to describe the development and rationale for some of the procedures used to test the toxicity of the extracts in the various biological test systems and to evaluate the applicability and compatability of the EP for such a testing protocol. None of the EP extracts of the seventeen solid wastes showed detectable mutagenic activity; although activity was found in a direct assay of an As-contaminated groundwater. To assess the relevance of the EP, samples of solid waste were taken from the landfill believed to be the source of the As in the groundwater sample, and extracted according to the EP protocol.

MATERIALS AND METHODS

A truly multidisciplinary team was necessary to evaluate properly the toxicity of extracts from solid wastes. It included environmental scientists, responsible for assessing the relevance of the extraction procedure and testing the effects of the extract on aquatic and terrestrial organisms, analytical chemists, responsible for detection, quantification, separation, and identification of the organic and inorganic toxic constituents, as well as a team of microbial biologists and geneticists trained in the development and interpretation of bioassays to detect indicators of mutagenicity and carcinogenicity. Each group has directed considerable effort into developing the necessary methods to accomplish their tasks. Thus, the following will be a short description of the protocol used by each; detailed description is available in the final report "Toxicity of Leachates" to be issued soon as a joint ORNL and EPA publication (Epler, et. al.[3]).

Extraction Procedure

The solid wastes were extracted using the proposed EP published in the December 18, 1978, Federal Register (43 FR 58956). Several vessels (plexiglass, Type 316 stainless steel, and glass) with certain modifications in engineering designs were used. Data recorded during the EP consisted of: 1) initial pH; 2) final pH; 3) amount of acetic acid added; and 4) electrical conductivity of the final extract. The final solid and liquid phases were separated by vacuum filtration (Millipore 0.45 μm pore size, type HA filter). Aliquots of the extract were distributed to the appropriate groups for chemical characterization and biotesting (aquatic and phytotoxic effects).

Chemical Characterization

Chemical characterization included identifying and quantifying the chemical constituents in the EP extracts and concentrating the organic components in the EP extract for mutagenesis biotesting. A macroreticular resin sorption technique (XAD-2 resin provided a direct 100-fold increase) was used to concentrate the organic constituents from the EP extracts. These were separated into nonpolar and polar fractions using a Florisil column. The nonpolar fraction was further divided on an alumina column using various eluting solutions (hexane, 6:1 hexane:benzene, 2:1 hexane:benzene and acetone) into a PCB-pesticide-monoaromatic-diaromatic-parafin fraction, a diaromatic fraction, a polyaromatic fraction, and a heteroaromatic fraction. The EP organic concentrates tested for mutagenesis were collected on the XAD-2 resin and eluted using cyclohexane. Atomic absorption spectroscopy (flameless graphite furnace) was used to determine the inorganic constituents in the EP extract.

As an alternative to the EP, a steam distillation procedure was developed to extract greater quantities of organics from selected solid wastes than those observed with the EP. The solid waste (100 g) in 250 ml of triply distilled water is refluxed so that the steam and an organic solvent (immiscible in water), which is heated in another vessel, co-condense; the aqueous and non-aqueous phases separate and return to their respective vessels. In this manner, organics in the solid wastes entrained in the steam can be separated from the aqueous phase without direct extraction of the waste with an organic solvent, and without filtration.

Aquatic Toxicity

The test organism, Daphnia magna, was used in acute (48 h) and chronic testing (28 d) procedures. Results of the acute tests, expressed in LC_{50}'s, represented the concentration of the EP extract that was lethal to 50% of the D. magna during the 48 hours of exposure. Chronic testing was carried out only at EP extract dilutions of 1:100 and 1:1000. The extracts were neutralized to pH 7 before testing. To evaluate the influence of acetic acid added in the EP, controls containing equivalent amounts of acetic acid and neutralized to 7.0 were used in conjunction with well-water controls.

Phytotoxicity

Short-term root elongation tests (48 and 72 h) using radish and sorghum and longer term seedling tests (2 and 3 weeks) using wheat and soybeans (response in dry weight of root and shoot) were used to evaluate the toxicity of EP extracts to plants. Extracts were diluted to various concentrations with distilled water for the root elongation tests and with a balanced nutrient solution for the seedling tests.

Mutagenicity

Three bioassays diagnostic for genetic activity were used to test the EP extracts and XAD-2 concentrates of the EP extracts for mutagenecity. They were: 1) the Salmonella/Microsome, 2) the Saccharomyces can^r/his^+ dual assay, and 3) the Repair Assay (Ames, McCann, and Yamasaki[1]; McCann et. al.[4]; Larimer, Ramey, Lijinsky, and Epler[5]).

RESULTS AND DISCUSSION

Extraction Procedure

Preliminary extractions were carried out in vessels made of plexiglass and Type 316 stainless steel; both designed as described in Federal Register, Vol. 43, No. 243. The plexiglass vessel was eliminated due to possible sorption of organics on the vessel walls as well as its incompatibility in testing solid wastes containing high concentrations of organic solvents. The stainless steel unit design was found to be unsatisfactory because of binding between the stirring blades and solid particles that caused overloading and eventual malfunction of the stirring motor. A modified version of the extraction equipment was designed and fabricated at ORNL. The new design integrated the type 316 stainless steel vessel with a high-torque, low rpm stirring motor with the stirring rod centered on a conical bearing at the bottom of the vessel. Sample grinding was the main problem encountered with this design. A stirrer with Teflon blades proved to be a satisfactory alternative.

Contamination by the Stainless Steel Vessel — Our data indicate that use of a stainless steel vessel likely contaminates EP extracts with Cr and Ni. For instance, distilled water blanks acidified to pH 3.5 with nitric acid contained significantly more Cd, Cr, Cu, Pb, Ni, and Pb than the same water elevated to pH 10 with NH_4OH. Acid washed sand (solid:water ratio 1:20) EP extracts contained significantly more Cr and Ni than distilled water blanks (Fig. 1), indicating that the abrasive action of course particles grinding against the vessel walls will likely enhance dissolution of Cr and Ni from the stainless steel vessel.

Extraction Variability — Each of the 17 solid wastes were extracted four times with

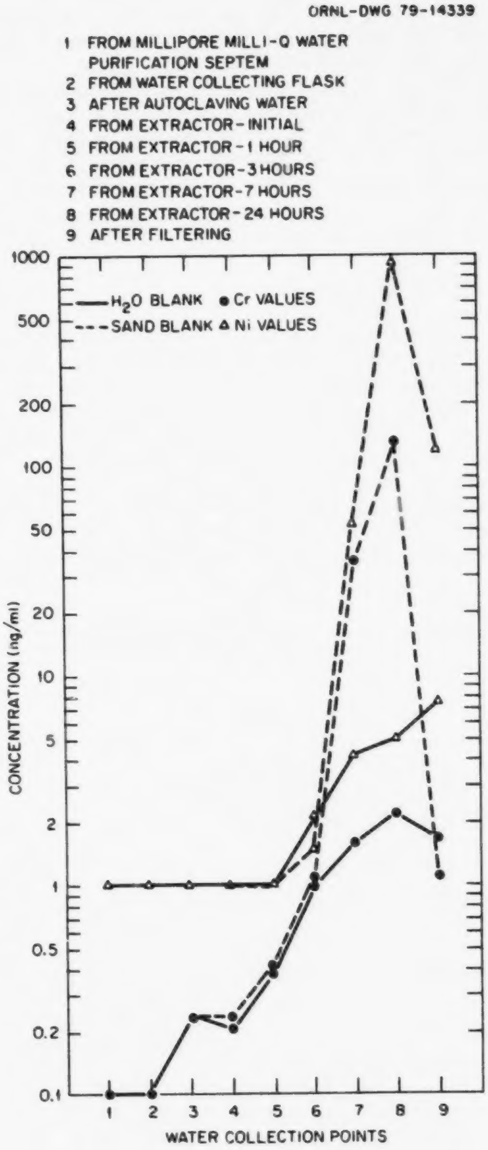

Figure 1. Higher concentrations of Cr and Ni were observed in EP extracts using acid washed sand than distilled water in a stainless steel extraction vessel with Teflon stirrer.

the EP and analyzed separately for Cr, Ni, and Ca. The coefficient of variation [CV = $(s/\bar{x})$ (100)] ranged from 7 to 83, 10 to 94, and 2 to 29% for Cr, Ni, and Ca, respectively. There did not appear to be a relationship between extraction variability and waste type. The variability associated with the analysis of Cr, Ni, and Ca at the reported concentrations needs to be verified. Considering the major constraints involved in interpreting what is a toxic concentration, (Is 10 times the primary drinking water standard really toxic in the environment?) the errors associated with the extraction variability appear to be a minor problem at CV's less than 100%.

Toxicity of Extracts

"Toxicity" of an EP extract is defined in this manuscript as 1) any extract in which the concentration of As, Ba, Cd, Cr, Pb, Hg, Se, or Ag was greater than ten times the EPA Primary Drinking Water Standard or 2) any extract that showed a positive test for toxicity in any of the bioassays (aquatic, phytotoxicity, or mutagenicity). A summary of the results is presented in Table 1. Omitted from this Table is the analysis for organic compounds. The following organics were not detected (limit of detection) in any of the extracts: PAH's (2 mg/ℓ), volatile organics (0.1 mg/ℓ), and pesticides (0.1 to 1 mg/ℓ). Quantities of PCB's detected ranged from 0.2 to 1.0 mg/ℓ but they probably represented contamination rather than originating from the waste. A concentration of 320 mg/ℓ of o-nitroaniline was measured in the As-groundwater sample and represented the only organic compound found in any of the samples that could be considered "toxic" based on RCRA classification.

Only four of the 17 solid wastes would not comply with the currently proposed RCRA regulations (43 FR 58950) on toxicity. These wastes (No.'s 2, 3, 8, and 9) had excessive metal concentrations in the EP extract. The others that showed positive signs of toxicity by the bioassay tests would only be considered toxic or hazardous if adequate tests could be developed that would reflect accurately the characteristics of that waste. One of the major objectives in this work was to identify the constraints in bioassay protocols using EP extracts so that reliable bioassays can be developed

TABLE 1. TOXICITY OF EP EXTRACTS FROM SOLID WASTES

Solid Waste	Metals	Bioassay[a]		
		Aquatic	Phytotoxicity	Mutagenicity
1. Soybean Process Cake	-	-	+	-
2. Metal Processing Waste	Cr	-	+	-
3. Plater's Waste	Cd, Cr	+	+	-
4. Raw Shale	-	-	+	-
5. Retorted Shale	-	-	+	-
6. Dye Waste	-	+	+	-
7. Textile Waste	-	-	+	-
8. Municipal Sewage Sludge	Cd	+	-	-
9. Power Plant No. 1 - Fly Ash	Cd	-	+	-
10. - Bottom Ash	-	-	+	-
11. - Scrubber Sludge	-	-	+	-
12. - Treated Scrubber Sludge	-	-	+	-
13. Power Plant No. 2 - Fly Ash	-	-	-	-
14. Fluidized Bed Residue	-	-	-	-
15. Gasification Bottom Ash No. 1	-	-	-	-
16. Gasification Bottom Ash No. 2	-	+	-	-
17. Gasification Bottom Ash No. 3	-	-	+	-
As-Contaminated Groundwater[b]	As, Cd	+	+	+

[a] + = toxicity; - = nontoxicity.

[b] Is not an EP extract but a groundwater sample furnished by EPA and concentrated on an XAD-2 column before testing for mutagenicity.

and used to effectively determine the hazards of solid wastes.

None of the EP extracts appear to be mutagenic based on these bioassays. Short-term assays often show negative results with certain heavy metals and classes of organic compounds known to be biologically toxic. However, in this case, the primary reason for the observed negative responses in the mutagenicity bioassays may be the inability of the EP to extract organics from the solid wastes. The acidic aqueous character of the EP would not favor the removal of nonpolar organics, particularly PAH's which are highly water insoluble and sorb tenaciously to solid surfaces in the suspension. Likewise, some carbon-14 labeled PAH's are known to be sorbed (>90%) on the filters used in the separation of the extract (Brown et. al.[2]). Thus, final judgment on the mutagenicity of these solid waste leachates should be deferred until scientific evidence indicates that the present EP or an alternative EP is free of artifacts peculiar to the EP itself. Environmental, biogeochemical conditions expected in groundwater from a landfill containing these wastes should be selected for in future modifications of the EP

The phytotoxicity tests showed positive signs of toxicity for 12 of the 17 EP extracts (Table 1). The waste was classified as toxic if statistically significant ($P<0.05$) reduction in growth (either in the root elongation or seedling growth tests) was observed with any of the plant species (radish, sorghum, wheat, or soybean) at any concentration of the EP extract (0.5 to 100%). A major and very serious constraint in interpretation of the phytotoxicity tests is the toxicity of acetic acid to plant growth. Growth reduction in seedling and root elongation tests were noted at 2.5×10^{-3} M acetic acid. The EP protocol requires adjustment to pH 5.0 using acetic acid during the 24 h extraction period (maximum amount of acetic acid allowed, 10^{-1} M). Thus, this phytotoxity bioassay reflects not only the inherent toxicity of the waste but in many instances the quantity of acetic acid required to maintain a pH of 5.0 during the EP. It appears that before phytotoxicity bioassays can be implemented as a reliable protocol to test toxicity of EP extracts, problems inherent in using acetic acid will have to be overcome.

Acetic acid in the EP also interferes in the interpretation of the aquatic bioassay. In this case, the acetic acid can reduce as well as enhance toxic responses. For example, acetate is an excellent carbon source for bacterial growth which in turn is a food supply for *D. magna*, the aquatic test organism. Thus, acetic acid additions in the EP can stimulate as well as reduce the growth and reproduction of *D. magna*. As with the phytotoxicity assays, problems associated with using acetic acid must be overcome before reliability can be placed on the aquatic assays.

As-Contaminated Groundwater

The As-contaminated groundwater appeared to be very toxic judging from the concentrations in the inorganic and organic analyses as well as from results of all the bioassays. To assess the significance of an EP, two solid waste samples were retrieved from this landfill along with additional groundwater samples during the fall of 1979. These samples of solid waste taken from the landfill are not intended to represent a scientifically well-defined sampling protocol describing the physicochemical character of the waste or its distribution in the landfill, but merely a first order estimate of the waste in its present form. Groundwater was sampled from three wells at increasing distances from the landfill.

Three extracting procedures were used to compare the dissolution of nitroaniline from the two solid waste samples (Table 2). The acidic, aqueous EP extracted as much nitroaniline as either the soxhlet or steam distillation procedures. Nitroaniline, though, is a highly water soluble organic compound and, as such, represents a best possible case for the EP. Earlier comparisons have indicated the EP to be considerably less effective than these two procedures in the extraction of high-molecular weight, low water soluble organic compounds. The low recovery of As in the aqueous phase of the steam distillate likely reflects the loss of organic arsenicals to the methylene chloride. These samples were expected to contain various phenylarsenic acids. The concentration of nitroaniline in the EP extract was significantly lower than the concentrations observed in the well water. Well water concentrations decreased with increasing distance from

TABLE 2. COMPARISON OF SOLID WASTE EXTRACTION PROCEDURES AND CONCENTRATIONS IN THE EP EXTRACT RELATIVE TO THAT IN GROUNDWATER NEAR LANDFILL

Extraction Procedure[a]	Nitroaniline	As
	Quantity Extracted mg/g	
Soxhlet	0.96 ± 0.17	-
Steam Distillation	0.90 ± 0.04	0.96 ± 0.00
EP	1.04 ± 0.07	3.06 ± 1.62
Groundwater and EP Extract	Concentration µg/ml	
Well No. 1	1320	151
Well No. 2	680	157
Well No. 3	440	92
EP	51 ± 1	153 ± 81

[a] Methylene chloride used as the solvent in the soxhlet and as the organic solvent in the steam distillation procedure; nitroaniline determined in organic phase of steam distillation procedure while As was determined in the aqueous phase. Averages and standard deviation from two separate solid waste samples.

the landfill, approximately 40, 60, and 80 meters for No. 1, 2, and 3 wells, respectively. Arsenic concentration in the well water did not vary as much with distance and was close to that observed in the EP extracts. With the limited data available, further comparisons regarding the significance of these concentrations with that observed in the EP extracts are simply speculation. However, it does represent the first step in assessing the usefulness of an EP.

CONCLUSIONS AND RECOMMENDATIONS

Acetic acid interferes in bioassays for aquatic and phytotoxic effects.

An extractor vessel made of glass or Teflon should be used in the EP rather than stainless steel to avoid possible heavy metal contamination (Cd, Ni, and Cr).

To eliminate the sorption of PAH's or other highly water-insoluble organics on the filter membrane, the suggested filtering procedure in the proposed EPA EP should be modified or replaced with an alternative method.

A comprehensive evaluation should be made correlating the properties of the EPA proposed EP extract (or an alternative EP) and authentic landfill leachates.

ACKNOWLEDGMENTS

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CHEMICAL SPECIATION OF FLUE GAS DESULFURIZATION WASTES

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ABSTRACT

In this study, a thermodynamic equilibrium model for evaluating the chemical speciation of constituents in FGD wastes was evaluated. This model was also used to characterize the distribution, migration trends, stability fields, and concentration levels of constituents in FGD wastes. The suitability and accuracy of the model was verified by comparing calculated results to analytical data and certain scientific considerations. The model was then utilized to determine the effects of various operational or chemical changes in the FGD system or sludge treatment system on the concentration and chemical form of the impurities of interest.

INTRODUCTION

Conventional environmental impact assessment of flue gas desulfurization (FGD) sludge disposal includes chemical analysis and identification of the total concentrations of constituents in the sludge and its leachate. However, environmental and public health effects of FGD waste disposal depends upon which chemical forms or species of the constituents are released to surrounding waters, and not necessarily on their total concentration.

Thermodynamic modeling provides a feasible means of obtaining contaminant species information in FGD wastes. A thermodynamic model can also be used to predict the migration trends of the constituents as the FGD waste ages, as well as to estimate the final constituent concentration in the FGD leachate (aged wastewater) without conducting expensive field monitoring. Modeling is also useful for predicting the effects of operational and chemical changes in the FGD wastes.

Many available techniques can be used to construct and interpret a chemical thermodynamic model (Brinkley[2], Brinkley[3], Butler[4], Crerar[5], Crerar[6], Feldman[7], Helgeson[8], Helgeson[9], Helgenson[10], Helgeson[11], Karpov[12], Lu[14], Morel[16], Naphtali[17], and White[20]). In this study, the equilibrium constant approach was selected. The equilibrium constant method involves solving the stoichiometric equations of various chemical species, which are subject to constraints imposed by the equilibrium constants as well as mass balance and charge balance relations. Diagrams, such as Eh-pH plots, ion-ratio plots, concentration-pH figures, and species distribution figures, are used to display the stability field and speciation results.

The thermodynamic model used in this study was verified for suitability and accuracy by the analytical results of various FGD sludge samples obtained from the Kansas City Power and Light La Cygne Power Station. The model was also operated over a wide range of operational and chemical changes to determine their impacts on the concentration and speciation of various solid and soluble species. The impacts of (1) changes in pH and ionic strength; (2) addition of lime, silicates, hydrogen sulfide, and phosphates to the sludge; (3) variation of chloride, sulfate, and borate levels; (4) addition of magnesium to the sorbent; and (5) sulfite oxidation, were all estimated using the model.

METHODOLOGY OF SPECIES ANALYSIS

The speciation model is constructed by the equilibrium constant approach. The actual mathematical equilibrium model involves a series of simultaneous equations which describe the various interactions among components of the system. In order to solve these equations simultaneously, the information on metal and ligand species, overall formation constants, solubility products (and/or Henry's constants), and activity coefficients must be compiled from the literature. A computer solution is necessary, as the expanded equations number in the hundreds. The resultant nonlinear equations are solved by Newton-Raphson iteration.(see Table 1)

Because the chemical composition of FGD waste can vary over an extremely wide range, this study focused on speciation at the lowest levels (ionic strength (I) = 0.05) and the highest levels (I = 0.8). All possible distributions of species are expected to be within this range. The general concentration ranges of constituents in FGD sludges and leachates are listed in Table 2.

SPECIATION OF CONSTITUENTS IN FGD WASTES

Fresh FGD Leachates

Modeling speciation of fresh FGD leachates require two simplifying assumptions: (1) equilibrium conditions among the soluble species can easily be reached; and (2) the rates of nucleation and dissolution of the solid species are extremely low. Thermodynamic modeling of fresh FGD leachates can therefore be performed as if no new solids were formed or dissolved in the system. Included in the model were 20 important metals, 13 important ligands and 155 possible complexes.

Calculation results indicate that the major ions (i.e., calcium, magnesium, potassium, and sodium) exist mainly as free ions. However, trace metals are complexed considerably in fresh FGD leachates. The speciation of calcium and cadmium at both low and high ionic strengths (I = 0.05 and I = 0.8) is shown in Figures 1 to 4 as examples. In general, chloride complexes may become the predominant species for cadmium, copper, lead, mercury, and zinc; borate complexes may become the predominant species for copper and lead; sulfite complexes may become the predominant species for cadmium and iron; and hydroxide complexes may become the predominant species for the trivalent metals, e.g., chromium and iron, mercury and zinc. In fresh FGD leachates, arsenic and selenium exist primarily as arsenate and selenite species. The predominance of a given species can be affected significantly by the pH level of leachate. The ionic strength (or, more specifically, the soluble levels of the related ligands) also plays an important role in the speciation of most constituents.

Aged FGD Wastes

The speciation of constituents in the solid and soluble phases of aged FGD wastes was computed with the assumption that the equilibrium condition among all the soluble and solid species had been reached. Due to the long contact period, it is generally quite possible that equilibrium conditions between solid and liquid phases can be reached in the aged FGD wastes. The calculated results for two elements (calcium and cadmium at I = 0.05) are shown in Figures 5 to 8 as examples. Results of other elements at selected conditions are summarized in Table 3.

Results show that sulfur dioxide removed from the flue gas reacts to form $CaSO_4 \cdot 2H_2O(s)$ and $CaSO_3 \cdot \frac{1}{2}H_2O(s)$ in the FGD sludge. In the aged sludge, carbonate solids may become the predominant species for cadmium, calcium (when pH is greater than 7), copper, lead (at pH greater than about 9), manganese (at pH greater than about 7.5), and zinc (at high ionic strength, and pH around 8). Hydroxide solids are the predominant species for chromium, iron, cadmium (at pH greater than 9), magnesium (at pH greater than 9), manganese (at pH greater than about 9), and zinc (at low ionic strength, and pH greater than about 9) in the aged sludge. Arsenic, mercury, and selenium exist primarily as elemental metals in the aged sludge. Aluminium forms predominantly phosphate solids at low pH, and oxide solids at high pH. In aged sludge, the molybdate and silicate solids are usually the predominant species for lead and zinc, respectively.

The predominant soluble species of constituents in the aged FGD leachates are similar to those found in fresh FGD leachates. However, the concentrations of these soluble species are generally decreased through aging, due to the nature of solids formed. The predominant soluble species, and their concentrations for each individual constitutent at two different ionic strengths, are shown in Table 3. In most cases, the predominant species alone

TABLE 1. GENERAL MODELS USED FOR SPECIATION CALCULATION

$$[M(i)_m L(j)_n] = \beta(i,j)_{nm} [M(i)_f]^m [L(j)_f]^n \cdot \frac{\gamma^m_{M(i)} \; \gamma^n_{L(j)}}{\gamma_{M(i)_m \, L(j)_n}}$$

$$[M(i)_f] = \frac{K_{M(i)_p L(j)_q} \cdot R_{M(i)_p L(j)_q} \cdot f_{M(i)_p L(j)_q}}{\gamma^p_{M(i)} \cdot \gamma^q_{L(j)} \; [L(j)_f]^q}$$

$$[L(j)_f] = \frac{K_{M(i)_u L(j)_v} \cdot R_{M(i)_u L(j)_v} \cdot f_{M(i)_u L(j)_v}}{\gamma^u_{M(i)} \cdot \gamma^v_{L(j)} \; [M(i)_f]^v}$$

$$\sum_{j=1}^{h} \sum_{p=1}^{a} \sum_{q=1}^{b} R_{M(i)_p L(j)_q} = 1$$

$$\sum_{i=1}^{g} \sum_{u=1}^{c} \sum_{v=1}^{d} R_{M(i)_u L(j)_v} = 1$$

$$\begin{aligned} [M(i)_T] = [M(i)_f] &+ \sum_{m=1}^{k} \sum_{n=1}^{l} \sum_{j=1}^{h} m \, [M(i)_m L(j)_n] \\ &+ \sum_{j=1}^{h} \sum_{p=1}^{a} \sum_{q=1}^{b} p \, [M(i)_p L(j)_q] \\ &+ \sum_{j=1}^{h} \sum_{u=1}^{c} \sum_{v=1}^{d} u \, [M(i)_u L(j)_v] \end{aligned}$$

$$\begin{aligned} [L(j)_T] = L(j)_f &+ \sum_{m=1}^{k} \sum_{n=1}^{l} \sum_{i=1}^{g} n \, [M(i)_m L(j)_n] \\ &+ \sum_{i=1}^{g} \sum_{p=1}^{a} \sum_{q=1}^{b} q \, [M(i)_p L(j)_q] \end{aligned}$$

(continued)

TABLE 1. (concluded)

$$+ \sum_{i=1}^{g} \sum_{u=1}^{c} \sum_{v=1}^{d} v \left[M(i)_u L(j)_v\right]$$

where:

$[M(i)_m L(j)_n]$ = concentration of complex $M(i)_m L(j)_n$ (in Molar)

$[M(i)_f]$ = free concentration of ith metal (in Molar)

$[L(j)_f]$ = free concentration of jth ligand (in Molar)

$[M(i)_T]$ = total concentration of ith metal in the system (in Molar)

$[M(i)_p L(j)_q]$ and $[M(i)_u L(j)_v]$ = concentration of solids $M(i)_p L(j)_q$ and $M(i)_u L(j)_v$ based on the solution volume (in Molar)

${}^{R}M(i)_p L(j)_q$ and ${}^{R}M(i)_u L(j)_v$ = mole fraction of solid or gas species for metal or ligand solids

i = metal species

j = ligand species

g = total number of metals

h = total number of ligands

k = maximum number of metals M(i) coordinate ligands L(j)

l = maximum number of ligands L(j) coordinate metals M(i)

a,b c and d = positive integers showing maximum number of the composition of metals or ligands in the solids or gases

$\beta(i,j)_{nm}$ = overall formation constant of complex $M(i)_m L(j)_n$

γ_x = thermodynamic activity coefficient of soluble species x, and

f_x = thermodynamic activity coefficient of solid (or gas) species x (in this study, assume $f_x \simeq 1$).

K = solubility products or Henry's constants.

TABLE 2. CONCENTRATION RANGES OF CONSTITUENTS IN FGD SLUDGES AND LEACHATES*

* References: Bornstein[1]; Leo[13]; Lunt[15]; Princiotta[18]; and SCS[19].

Constituents	Concentration in Scrubber Liquors mg/l (except pH)	Molar	Total Concentration (Sludge & Liquor) (Molar)
Aluminum	0.03-0.3	$10^{-5.95}$-$10^{-4.95}$	$10^{-5.95}$-$10^{-4.95}$
Arsenic	<0.004-0.3	$10^{-7.27}$-$10^{-5.40}$	$10-^{3.88}$-$10^{-3.87}$
Beryllium	<0.002-0.14	$10^{-6.65}$-$10^{-4.81}$	$10^{-3.97}$-$10^{-3.91}$
Boron	8.0-46	$10^{-3.13}$-$10^{-2.37}$	$10^{-2.57}$-$10^{-2.21}$
Cadmium	0.004-0.11	$10^{-7.44}$-$10^{6.01}$	$10^{-4.97}$-$10^{-4.97}$
Calcium	520-3,000	$10^{-1.89}$-$10^{-1.12}$	$10^{0.19}$-$10^{0.21}$
Chromium	0.01-0.5	$10^{-6.72}$-$10^{-5.02}$	$10^{-4.03}$-$10^{-3.99}$
Cobalt	<0.19-0.7	$10^{-5.77}$-$10^{4.92}$	$10^{-2.87}$-$10^{-2.86}$
Copper	<0.002-0.2	$10^{-7.50}$-$10^{5.50}$	$10^{-4.18}$-$10^{-4.16}$
Iron	0.02-8.1	$10^{-6.45}$-$10^{-3.84}$	$10^{-0.57}$-$10^{-0.57}$
Lead	0.01-0.4	$10^{-7.32}$-$10^{-5.71}$	$10^{-4.69}$-$10^{-4.65}$
Magnesium	3.0-2,750	$10^{-3.91}$-$10^{-0.95}$	$10^{-3.91}$-$10^{-0.95}$
Manganese	0.09-2.5	$10^{-5.79}$-$10^{-4.34}$	$10^{-3.46}$-$10^{-3.41}$
Mercury	0.0004-0.007	$10^{-8.70}$-$10^{-6.46}$	$10^{-5.83}$-$10^{-5.74}$
Molybdenum	0.91-6.3	$10^{-4.71}$-$10^{-4.18}$	$10^{-3.95}$-$10^{-3.80}$
Nickel	0.05-1.5	$10^{-6.07}$-$10^{-4.59}$	$10^{-4.06}$-$10^{-3.95}$
Potassium	5.9-32	$10^{-3.82}$-$10^{-3.09}$	$10^{-1.89}$-$10^{1.87}$
Selenium	< 0.001-2.2	$10^{-7.90}$-$10^{-4.56}$	$10^{-4.58}$-$10^{-4.27}$
Silicon	0.2-3.3	$10^{-5.15}$-$10^{-3.93}$	$10^{-5.15}$-$10^{-3.93}$
Silver	0.005-0.6	$10^{-7.33}$-$10^{-5.25}$	$10^{-4.56}$-$10^{-4.48}$
Sodium	14-2,400	$10^{-3.21}$-$10^{-0.98}$	$10^{-1.36}$-$10^{-0.83}$
Tin	3.1-3.5	$10^{-4.58}$-$10^{-4.53}$	$10^{-3.06}$-$10^{-3.06}$
Vanadium	< 0.001-0.67	$10^{-7.71}$-$10^{-4.88}$	$10^{-3.45}$-$10^{-3.43}$
Zinc	0.01-0.35	$10^{-6.82}$-$10^{-5.27}$	$10^{-3.58}$-$10^{-3.57}$
Carbonate	41-150 (as $CaCO_3$)	$10^{-3.39}$-$10^{-2.82}$	$10^{-0.20}$-$10^{-0.20}$
Chloride	420-4,800	$10^{-1.93}$-$10^{-0.87}$	$10^{-1.93}$-$10^{-0.87}$
Fluoride	0.07-10	$10^{-5.43}$-$10^{-3.28}$	$10^{-2.2}$-$10^{-2.17}$
Sulfite	0.8-3,500	$10^{-5.00}$-$10^{-1.36}$	$10^{-0.24}$-$10^{-0.21}$
Sulfate	720-10,000	$10^{-2.12}$-$10^{-0.98}$	$10^{-0.45}$-$10^{-0.35}$
Phosphate	0.03-0.41	$10^{-6.50}$-$10^{-5.36}$	$10^{-6.50}$-$10^{-5.36}$
pH	3.04-10.7	$10^{-3.04}$-$10^{-10.7}$	$10^{-3.04}$-$10^{-10.7}$
Ionic Strength	---	0.05-0.80	0.05-0.80

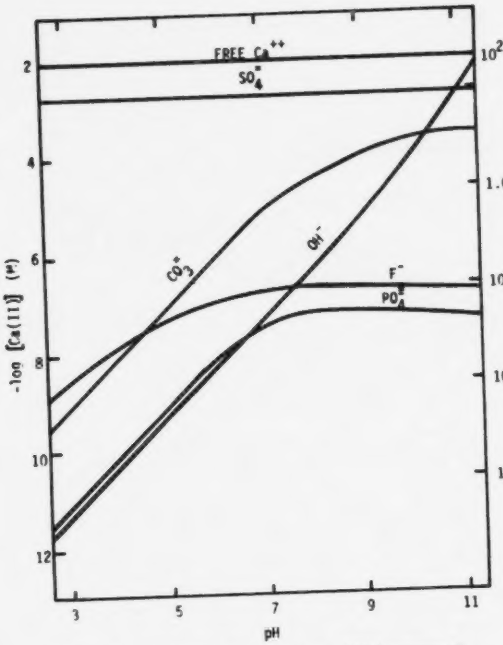

Figure 1. Speciation of Ca in fresh FGD leachate at $I = 0.05$, $[Ca_T] = 10^{-1.89}M$.

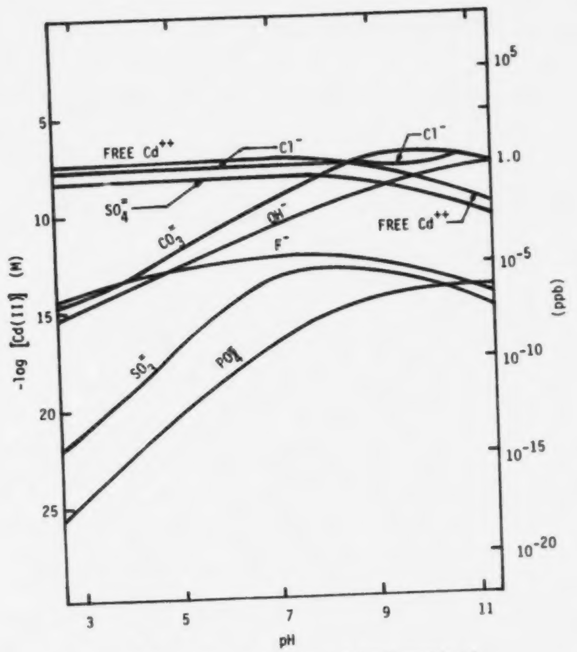

Figure 3. Speciation of Cd in fresh FGD leachate at $I = 0.05$, $[Cd_T] = 10^{-7.44}M$.

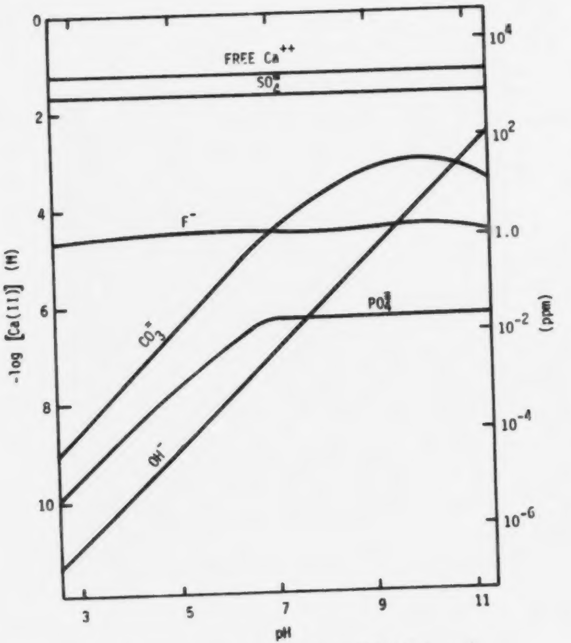

Figure 2. Speciation of Ca in fresh FGD leachate at $I = 0.8$, $[Ca_T] = 10^{-1.12}M$.

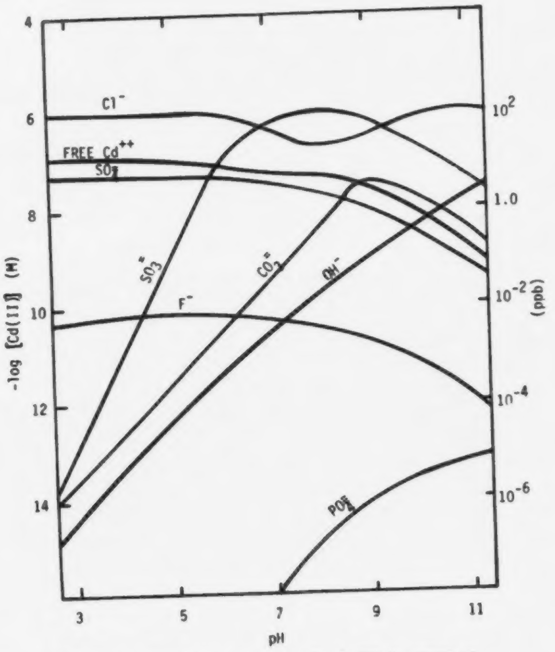

Figure 4. Speciation of Cd in fresh FGD leachate at $I = 0.8$, $[Cd_T] = 10^{-6.01}M$.

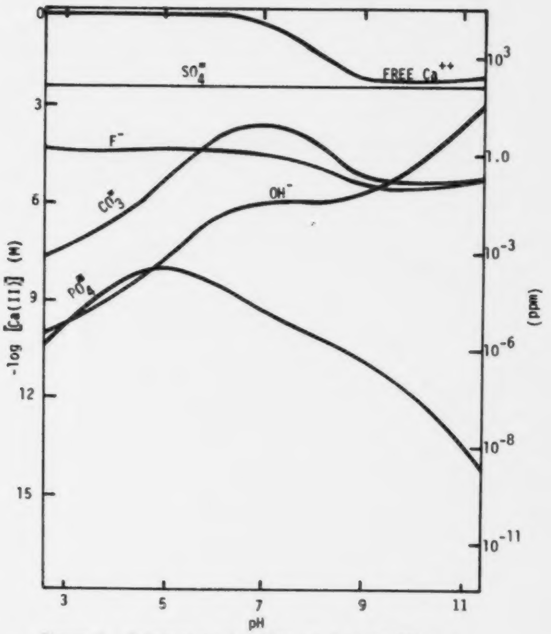

Figure 5. Speciation of soluble Ca in aged FGD waste at I=0.05, original $[Ca_T] = 10^{0.19}M$

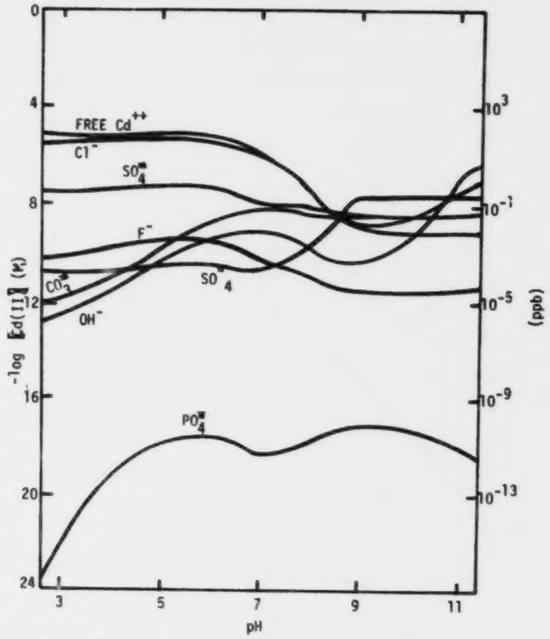

Figure 7. Speciation of soluble Cd in aged FGD wastes at I = 0.05, original $[Cd_T] = 10^{-4.97}M$

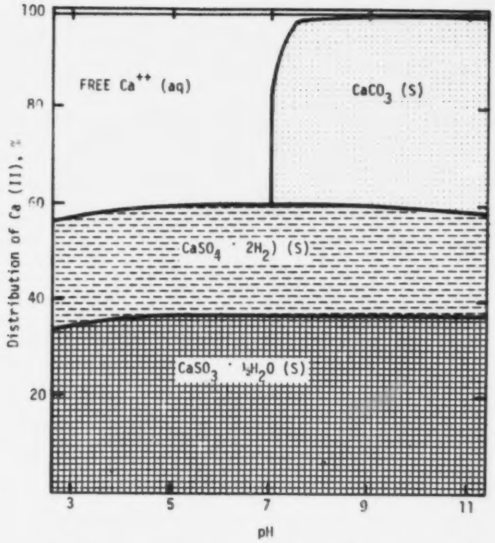

Figure 6. Primary distribution of Ca in aged FGD wastes at I = 0.05, original $Ca_T = 10^{0.19}M$

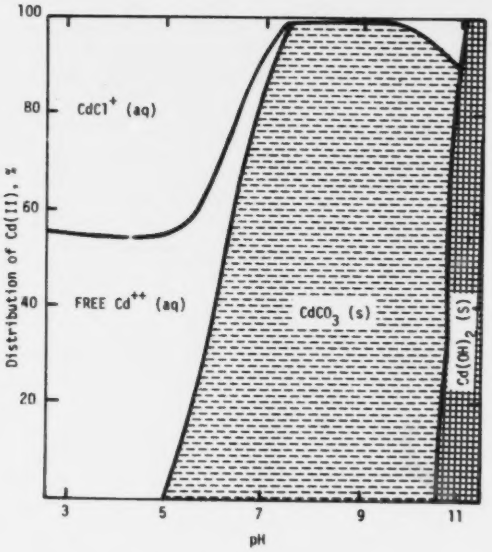

Figure 8. Primary distribution of Cd in aged FGD wastes at I = 0.05, original $Cd_T = 10^{-4.97}M$

TABLE 3. PREDOMINANT SPECIES OF CONSTITUENTS IN AGED FGD SLUDGE

Constituent	Ionic Strength	Predominant Solid Species*			Predominant Soluble Species*		
		pH = 5	pH = 7	pH = 9	pH = 5	pH = 7	pH = 9
Al	0.05	$Al(H_2PO_4)(OH)_2$	$Al(H_2PO_4)(OH)_2$	$Al_2O_3 \cdot 3H_2O$	$AlF_2^+(6.04)$	$Al(OH)_3(6.26)$	$Al(OH)_3(5.95)$
	0.8	$Al(H_2PO_4)(OH)_2$	$Al(H_2PO_4)(OH)_2$	$Al_2O_3 \cdot 3H_2O$	$AlF_2^+(5.05)$	$Al(OH)_3(6.89)$	$Al(OH)_3(5.36)$
As	0.05	As^o	As^o	As^o	$H_2ASO_4^-(8.03)$	$HAsO_4^{-2}(11.23)$	$HAsO_4^{-2}(8.82)$
	0.8	As^o	As^o	As^o	$H_2AsO_4^-(7.51)$	$HAsO_4^{-2}(10.87)$	$HAsO_4^{-2}(10.91)$
Cd	0.05	$CdCO_3$	$CdCO_3$	$Cd(OH)_2$	$Cd^{+2}(5.23)$	$Cd^{+2}(6.03)$	$Cd(SO_3)_2^{-2}(7.72)$
	0.8	$CdCO_3$	$CdCO_3$	$Cd(OH)_2, CdCO_3$	$CdCl^+(5.12)$	$CdCl^+(5.13)$	$CdClOH(6.07)$
Ca	0.05	$CaSO_3 \cdot \frac{1}{2}H_2O$, $CaSO_4 \cdot 2H_2O$	$CaSO_3 \cdot \frac{1}{2}H_2O$, $CaSO_4 \cdot 2H_2O$	$CaCO_3, CaSO_3 \cdot \frac{1}{2}H_2O$, $CaSO_4 \cdot 2H_2O$	$Ca^{+2}(.21)$	$Ca^{+2}(.53)$	$Ca^{+2}(2.19)$
	0.8	$CaSO_3 \cdot \frac{1}{2}H_2O$, $CaSO_4 \cdot 2H_2O$	$CaSO_3 \cdot \frac{1}{2}H_2O$, $CaSO_4 \cdot 2H_2O$	$CaCO_3, CaSO_3 \cdot \frac{1}{2}H_2O$, $CaSO_4 \cdot 2H_2O$	$Ca^{+2}(.25)$	$Ca^{+2}(.32)$	$Ca^{+2}(2.0)$
Cr	0.05	$Cr(OH)_3$	$Cr(OH)_3$	$Cr(OH)_3$	$CrOH^{+2}(4.13)$	$Cr(OH)_2^+(4.76)$	$Cr(OH)_4^-(4.03)$
	0.8	$Cr(OH)_3$	$Cr(OH)_3$	$Cr(OH)_3$	$Cr(OH)_2^+(5.0)$	$Cr(OH)_2^+(4.72)$	$Cr(OH)_4^-(3.99)$

TABLE 3. (Continued)

Constituent	Ionic Strength	Predominant Solid Species*			Predominant Soluble Species*		
		pH = 5	pH = 7	pH = 9	pH = 5	pH = 7	pH = 9
Cu	0.05	$Cu_2CO_3(OH)_2$	$Cu_2CO_3(OH)_2$	$Cu_2CO_3(OH)_2$	$CuB(OH)_4^+$(15.38)	$Cu(B(OH)_4)_2$(16.78)	$Cu(B(OH)_4)_2$(16.9)
	0.8	$Cu_2CO_3(OH)_2$	$Cu_2CO_3(OH)_2$	$Cu_2CO_3(OH)_2$	$CuB(OH)_4^+$(14.99)	$Cu(B(OH)_4)_2$(16.09)	$Cu(B(OH)_4)_2$(16.4)
Fe	0.05	$Fe(OH)_3$	$Fe(OH)_3$	$Fe(OH)_3$	$Fe(OH)_2^+$(7.16)	$Fe(OH)_2^+$(9.16)	$Fe(OH)_4$(10.07)
	0.8	$Fe(OH)_3$	$Fe(OH)_3$	$Fe(OH)_3$	$FeSO_3^+$(6.98)	$Fe(OH)_2^+$(9.12)	$Fe(OH)_4^-$(8.96)
Pb	0.05	$PbMoO_4$	$PbMoO_4$	$PbMoO_4$	Pb^{+2}(5.80)	$PbB(OH)_4^+$(5.82)	$Pb(B(OH)_4)_3^-$(7.14)
	0.8	$PbMoO_4$	$PbMoO_4$	$PbMoO_4.PbCO_3$	$PbCl^+$(5.67)	$PbB(OH)_4^+$(5.44)	$Pb(B(OH)_4)_3^-$(5.55)
Mg	0.05	--†	--†	$Mg(OH)_2$	Mg^{+2}(3.91)	Mg^{+2}(3.92)	Mg^{+2}(4.16)
	0.8	--†	--†	$Mg(OH)_2$	Mg^{+2}(0.95)	Mg^{+2}(.95)	Mg(1.13)
Mn	0.05	--†	--†	$MnCO_3$	Mn^{+2}(3.49)	Mn^{+2}(3.49)	$MnSO_4$(4.10)
	0.8	--†	--†	$Mn(OH)_2,MnCO_3$	Mn^{+2}(3.56)	Mn^{+2}(3.56)	Mn^{+2}(4.33)
Hg	0.05	Hg^0	Hg^0	Hg^0	$HgCl_2$(22.1)	$HgCl_2$(20.4)	$Hg(OH)_2$(17.9)
	0.8	Hg^0	Hg^0	Hg^0	$HgCl_3^-$(19.9)	$HgCl_3^-$(18.2)	HgClOH(17.0)

TABLE 3. (Concluded)

Constituent	Ionic Strength	Predominant Solid Species*			Predominant Soluble Species*		
		pH = 5	pH = 7	pH = 9	pH = 5	pH = 7	pH = 9
K	0.05	--†	--†	--†	K^+(1.89)	K^+(1.89)	K^+(1.93)
	0.8	--†	--†	--†	K^+(1.87)	K^+(1.87)	K^+(1.91)
Se	0.05	Se^0	Se^0	Se^0	$HSeO_3^-$(28.6)	$SeO_3^=$(18.2)	$SeO_3^=$(6.19)
	0.8	Se^0	Se^0	Se^0	$HSeO_3^-$(28.6)	$SeO_3^=$(18.2)	$SeO_3^=$(6.19)
Na	0.05	--†	--†	--†	Na^+(1.36)	Na^+(1.36)	Na^+(1.37)
	0.8	--†	--†	--†	Na^+(0.83)	Na^+(0.83)	Na^+(.85)
Zn	0.05	--†	$ZnSiO_3$	$Zn(OH)_2$	Zn^{+2}(3.63)	Zn^{+2}(3.65)	$ZnSO_4$(5.67)
	0.8	$ZnSiO_3$	$ZnSiO_3$	$ZnSiO_3$, $ZnCO_3$, $Zn(OH)_2$	Zn^{+2}(3.84)	Zn^{+2}(4.06)	$Zn(OH)_2$(5.9)

Note: Values in parenthesis indicate the -log molar concentration.

*If one species accounts for less than 50 percent of the total concentration, then more than one species will appear for each condition.

†-- indicates that there is no stable solid or that the stable solid is in complex forms (e.g., complex silicates).

will account for a major portion of the concentration of each constituent in FGD leachates. Therefore, knowing the predominant solid and soluble species, the total soluble concentration of a constituent in FGD leachate can be easily calculated without the aid of the computer.

MODEL VERIFICATION

The thermodynamic model was verified by checking the model results against both analytical data and certain theoretical considerations.

Evaluations of the model in relation to analytical data, was performed by comparing the known soluble concentrations of constituents in aged FGD wastes to those predicted by the model. As summarized in Table 4, the calculated results for aluminum, arsenic, boron, cadmium, cobalt, copper, iron, manganese, mercury, potassium, selenium, sodium, and zinc, either approach or are very close to the concentration levels experienced in the field. For other elements (specifically calcium, chromium, fluoride, lead, and magnesium), the model was not as effective. The low levels of calcium predicted by the model are due primarily to the interaction of calcite with the Ca^{2+}-CO_3^{2-} and Ca^{2+}-SO_3^{2-} complexes in the model. The high levels of chromium and lead calculated by the model are due to the inclusion of hydroxide and carbonate complexes in the model. For fluoride and magnesium, the discrepancy may be caused by certain unsuitable solids included in the model. The discrepancies may be due to (1) errors in the stability constants and/or activity coefficients; (2) the effects of other mechanisms, such as adsorption by hydroxide solids or clay minerals; and (3) the effects of kinetic constraints.

An evaluation of the thermodynamic model was also performed according to scientific considerations. In general, the model results behave in accordance with basic chemical and thermodynamic principles, including the effects of changing pH, Eh, and ligand levels.

EFFECTS OF FGD SYSTEM AND SLUDGE VARIABLES ON CHEMICAL SPECIATION

For the purpose of selecting a sludge treatment or disposal procedure, it is useful to observe the possible beneficial or adverse effects of operational or chemical changes in an FGD system on sludge speciation. The chemical changes studied here include those of pH, ionic strength, chloride concentration, borate concentration, sulfate concentration, and sulfite oxidation. The operational changes studied were limited to the addition of lime, silicates, hydrogen sulfide, phosphates, and magnesium to the FGD system. Due to the sizable amount of results, details will not be described here. Following sections only give the qualitative descriptions of the results.

A change in pH can influence the direction of the alteration processes, e.g., dissolution, precipitation, adsorption, and complexation, in any chemical system. In general, a pH increase in the FGD waste system tends to dissolve more elemental constituents, e.g, $As^{o}(s)$, $Hg^{o}(\ell)$, and $Se^{o}(s)$, and to transform some of the carbonate, phosphate, or other solids into hydroxide solids, thus affecting the concentration of soluble constituents. A pH change may also affect the ligand concentrations, and thereby change the concentration of soluble constituents.

The overall effects of pH on the total constituent concentration depend on the solubility constants of the new solids formed, the new ligand concentrations, and the formation constants of the complexes. For example, a high pH level can increase total soluble mercury and selenium, and yet decrease most of the other bivalent trace metals. For trivalent metals such as chromium and iron, the minimum soluble constituent concentrations occur in the neutral pH region.

Although a change in ionic strength in the FGD waste can affect the stability constants, its effect on the soluble levels of constituents, or on the stability fields of various solids, are usually negligible if their related ligand levels are unchanged. The soluble chloride concentration of the FGD waste is a very important factor in determining the total soluble level of cadmium, copper, lead, mercury, and zinc. Variations in borate concentrations have an impact primarily on total soluble copper and lead concentrations. The soluble sulfate concentration may affect the total soluble calcium, magnesium, cadmium, and zinc concentrations. In general, if the total soluble levels of the above-mentioned ligands (e.g., chloride, borate, and sulfate) are known, the total soluble metal concentrations in the aged FGD leachates can be approximated without extensive

TABLE 4. VALIDITY OF THE THERMODYNAMIC MODEL FOR THE PREDICTION OF FGD SLUDGE SPECIATION*

Constituent	Validity of Model	Reason for Discrepancy
Al	Excellent	
As	Good	
B	Excellent	
Cd	Excellent	
Ca	Not applicable	Form strong $CaCO_3(s)$ when $pH > 7$
Cr	Not applicable	Form strong Cr^{3+}-OH^- complexes
Co	Good	
Cu	Excellent	
F	Not applicable	Solubility controlling solid unknown
Fe	Good	
Pb	Not applicable	Form strong Pb^{2+}-CO_3^{2-} & Pb^{2+}-OH^- complexes
Mg	Not applicable	Solubility controlling solid unknown
Mn	Excellent	
Hg	Excellent	
K	Good	
Se	Good	
Na	Good	
Zn	Excellent	

* Based on comparison of modeling results with Kansas City Power and Light FGD sludge analysis.

computation.

With regard to operational changes, sulfite oxidation may reduce the concentration of sulfite complexes and increase the concentration of sulfate complexes, but will have very little impact on the total soluble concentration of most metals. The most significant effect of sulfite oxidation is the transformation of $CaSO_3 \cdot \frac{1}{2}H_2O(s)$ to $CaSO_4 \cdot 2H_2O(s)$ or $CaCO_3(s)$, depending on pH levels. This transformation may affect the soluble levels of arsenic, mercury, and selenium if the redox potential is controlled by sulfate/sulfite species.

The addition of lime to the FGD sludge has been employed in pozzolanic fixation processes for the purpose of improving the engineering properties of the dewatered sludge. However, the model shows that lime addition may have an adverse effect on constituent solubility. The addition of lime to FGD wastes may reduce the total soluble levels of certain constituents such as arsenic and manganese. However, the total soluble levels of most other trace toxic metals, such as cadmium, chromium, copper, lead, mercury, selenium, and zinc, increase in aged FGD wastes following lime addition. This may actually increase the potential for environmental damage, should the concentration increase outweigh the dilution factor decrease which results from permeability reduction.

The addition of silicates may reduce the total soluble aluminum and zinc concentrations, but other elements studied are virtually unaffected.

Phosphate addition will only reduce two soluble major ions (calcium and magnesium) while increasing the soluble cadmium level. Phosphate itself is also a water pollutant, so the addition of phosphates is not recommended for the treatment of FGD leachates.

Hydrogen sulfide addition may reduce the soluble concentrations of trace metals substantially. This operational change, however, may not be desirable for an FGD system for two reasons: (1) hydrogen sulfide itself is a pollutant, and (2) the diffusion of oxygen into the sludge, followed by the oxidation process, will eventually return the soluble metals to their original concentrations.

Magnesium has been shown to improve the efficiency of wet FGD systems; the use of high magnesium reagents could therefore become commonplace. The model shows that, in general, the magnesium addition will not significantly affect the total soluble levels of most constituents.

CONCLUSIONS

Thermodynamic modeling of chemical speciation in FGD waste has shown that waste constituents can exist in a wide variety of chemical forms or species. The predominance and concentration of any particular chemical species are influenced by chemical factors such as pH, Eh, ionic strength, and total concentrations of ligands and metals in the system. Although the FGD chemical systems are extremely complex, the speciation of their elemental constituents can be quantified by calculation with reasonable accuracy.

Knowledge of the relative distribution of constituent species in the FGD system is useful for (1) the evaluation of general toxicity, and (2) predicting the migration of the constituent in the environment. When assessing the potential impacts of FGD sludge leachate on groundwater, examination of data from aged FGD wastes is most appropriate. Most in-situ FGD sludges have a low permeability (10^{-4} to 10^{-10} cm/sec) which provides months to years of contact time between leachate and sludge. During this period, various chemical species in the FGD waste (either in the solid or soluble phases) would gradually approach equilibrium. Unfortunately, there is a lack of documented information relating to the chemical species present in aged FGD waste. Therefore, the thermodynamic model can be useful for prediction both the concentrations of various species, and the total soluble concentrations of constituents in aged FGD waste. The background required for the calculation need include no more than the total levels of the constituents in the fresh FGD waste. This thermodynamic approach could provide a considerable cost saving over the traditional field survey. The thermodynamic model discussed here can also be used to predict solid or soluble species changes, and changes in the levels of total soluble constituents caused by operational or chemical factors.

The thermodynamic model employed in this study was found to be inaccurate when predicting the speciation of calcium, chromium, fluoride, lead, and magnesium. The disparity may have been caused by several factors, including adsorption by various solids or the kinetic constraints of the reactions. The speciation of other constituents, such as aluminum, arsenic cadmium, boron, cobalt, copper, iron, manganese, mercury, potassium, selenium, sodium, and zinc, showed very close correlation with the analytical results. More study is therefore suggested to (1) verify the model against different types of FGD wastes, and (2) include more of the controlling factors in the model.

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INTERPRETING RESULTS FROM SERIAL BATCH EXTRACTION TESTS OF WASTES AND SOILS

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ABSTRACT

It has been established that a graded serial batch extraction method is very useful for studying the leachability of industrial wastes and for determining the retention characteristics of soils. A correlation between waste and soil extraction volumes and the time of leaching in columns or in the field allowed developing a method for the accelerated testing of wastes and soils. Proper interpretation of the results yields a real-time analysis of what is occurring in the waste and underlying soils as the leaching progresses. Applications of the data and methods of presenting it in graphical and tabular form are demonstrated and discussed.

BACKGROUND

CONTROLLED EXPERIMENTS ARE NECESSARY

Samples taken in the field have some value for making predictions of waste leachability and the migration of hazardous ions through soil. However, the observations are limited to only those wastes which have actually been dumped and even then to just certain combinations of waste and soil types, waste-to-soil ratios, etc. In the field, variables are not readily changed to determine their effect and this lack of flexibility limits the examination to relatively few factors. Many variables are completely out of the control of the experimenter. Thus, predictions made from these types of studies may apply to a relatively limited range of industrial situations.

Laboratory studies have the advantage of allowing more control over a wider range of experimental conditions. But they also have the potential disadvantage that significant field variables may be excluded because of the difficulty in simulating complex field conditions or because of improper experiment design. It is necessary to include those variables active in the field which have a statistically significant effect upon the leaching of substances from a waste and/or the passage of these substances through soils, and to exclude or minimize variables that might be introduced by the experimental setup. If all of the controlling factors are not varied to establish their effects and if they are not included at proper levels, the empirical equations derived from this data may not be reliable in making predictions for situations where these variables are involved. It may be necessary to run preliminary experiments to see which variables have significant enough effects to merit including them in the final experimental plan. (Theoretical models may be of some help in identifying potential factors, but they are not reliable enough for making predictions in complex physical-chemical situations without experimentally-determined constants, coefficients, and/or exponents capable of compensating for an incomplete knowledge of the controlling variables and their interrelationships.)

There are two principal laboratory approaches for measuring the leachability of wastes and the migration of hazardous substances through soil. These are batchwise extractions and the continuously-leached column method, both of which are discussed below.

CONTINUOUSLY LEACHED COLUMNS VERSUS BATCH EXTRACTIONS

The migration of chemical substances through soil is usually studied in the laboratory using columns packed with soil to a predetermined bulk density (usually approximating the field density of the undisturbed soil). These soil columns are challenged with a solution extracted from a waste by water or by some other solvent such as municipal landfill leachate, or the soil is treated with simple solutions containing the ion under study. A useful configuration is shown in Figure 1 along with illustrative plots of the data obtained.

Continuously-leached column experiments provide information as to the ability of a soil to remove chemical substances from a waste extract. However, an important limitation of this method is the time and effort required to obtain and analyze a sufficient number of samples to make predictions of migration rates and toxic hazards. This usually requires months and may even take years, depending upon the flow rate of the leaching solution through the columns. The information obtained from relatively short-term column studies cannot be relied upon to describe what will occur during years of leaching.

When setting up experiments of this type, an investigator is faced with the problem of selecting values for each experimental parameter such as leaching solvent flow-rate, head pressure, soil bulk density, column diameter, waste-to-soil ratio, etc. The choice of these values may not all be entirely arbitrary, but a given set will yield results which probably apply only to that particular combination of conditions and the experiment may not be very useful for making general predictions. In addition, column experiments are cumbersome and do not readily lend themselves to changes in the levels of the experimental parameters. Thus, they are slow and relatively limited in applicability.

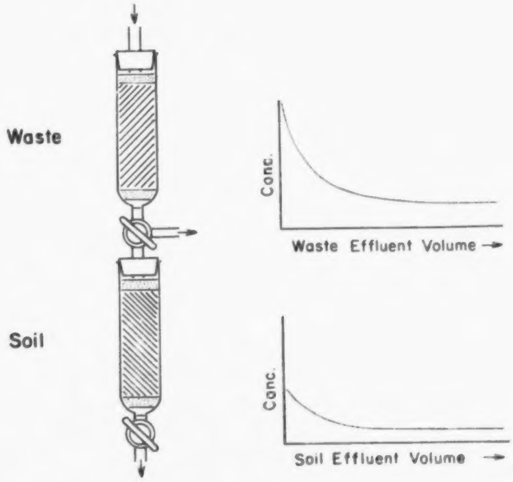

Figure 1. Continuously Leached Columns and Associated Output Plots

If an experimental approach were available which is more rapid and more versatile than the usual column leaching methods, a wider range of environmental conditions could be investigated, thereby more completely describing the behavior of a waste deposited on a soil. This would also make it more practical to use factorial experiment designs. Factorial experiments allow making predictions without sacrificing reliability even in the presence of interaction between multiple variables. (Interaction exists when the effect of one factor is dependent upon the level another factor. This introduces error into the results of classical, vary-one-factor-at-a-time experimentation). A fast method would also allow making timely determinations, on demand, for each specific situation.

In previous studies of the leachability of certain metals from a number of industrial wastes and the migration of these metals through soils, this laboratory used continuously-leached columns. A batch method was employed to rapidly screen soils for their ability to remove these metals from the waste leachate (1). This information was then used to select soils for more detailed column studies. While examining the data, it became apparent that properly designed batch studies of the leaching of both waste and soil could provide much of the same information obtained from column studies. However, no adequate information was available as to the correlation between batch extractions and continuously-leached columns of industrial wastes and soils. Therefore, samples of the industrial wastes used in the continuously-leached column studies were leached using a serial batch extraction procedure. It was found that the weights of toxic metals extracted from the wastes batchwise compared well to the column leaching (2) even though substantially greater amounts of water were present (200 to 4,800 percent versus less than 50 percent). Besides this, the results were obtained by the serial batch extraction method in only a small fraction of the time required by the column method. The serial batch method was experimentally much simpler, and it was concluded that this approach would permit the rapid investigation of the effect of a wide variety of environmental factors such as freeze/thaw and drying/resaturating cycles and similar variables that would be difficult to include in column studies.

Other investigators have used batch soil methods to study the removal of certain chemicals from waste extracts or municipal landfill leachate (3-6) and obtained results that compared reasonably well with column experiments. However, their experiments either did not allow for the changes in the waste extract composition as the waste depleted, for the further change as the extract contacted each increment of soil, and/or for the continually changing conditioning of each increment of soil, a change which depends both upon the leaching time and the soil depth.

CORRELATING CONTINUOUS AND BATCHWISE LEACHING(2)

The data obtained from continuously-leached columns may be presented in several ways. One technique is to plot the concentration of the chemical of interest found in the waste or soil column samples, versus the cumulative volume through the column. The common way of expressing the cumulative volume is to use the cumulative pore volume calculated for the type and weight of soil employed. However, changing the kind or amount of soil will change the scale of the cumulative volume axis when pore volume is employed. Figure 2 is an example showing the difference obtained with different pore volumes (in this case 40 and 60 mililiters). The corresponding total volume in milliliters is appended for comparison.

It often is not practical or possible to determine a pore volume for a waste because of its physical form (heterogeneous suspension, liquid, etc). This problem was circumvented by using the soil column pore volume as the measure of liquid volume through the waste. It allowed correlating the waste-column output with the soil-column results in a given set of experiments. However, instead of using the soil pore volume as the principal plotting parameter, it is much more flexible to plot the observed concentration of a chemical in an extract versus the cumulative milliliters of leaching solvent per gram of waste or soil, as shown in Figure 3. This makes the scaling independent of soil type, soil sample weight, and waste-to-soil ratio and allows the direct comparison of many different designs of experiments. It normalizes the results so they can be more readily correlated to a range of field conditions. The areas under the curves represent the total weight of a chemical extracted per gram of waste or soil. The weights thus obtained can be used to calculate attenuation or penetration factors for the soil.

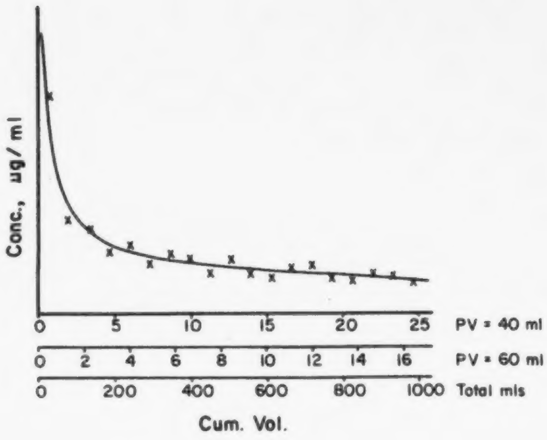

Figure 2. Differences in Scales used to Plot Cumulative Volume.

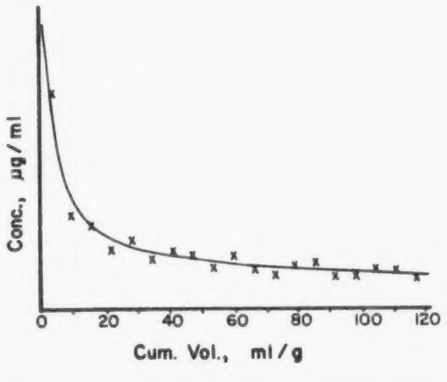

Figure 3. Normalization of Cumulative Volume using Milliters Per Gram

These considerations make it possible to correlate batch and continuously-leached column experiments. Batchwise extractions can be related to continuously-leached columns by recognizing that continuous leaching is equivalent to running a series of discrete extractions spaced by the frequency of collecting the effluent sample. Figure 4 shows that the concentration of a substance in the periodic column samples can be plotted to represent the average for that sampling period. Thus, samples from the continuous leaching of a column correspond to sequential batchwise extractions by volumes of extractant equal to the volume passing through a column between the taking of samples.

When extracting a batch of waste or soil, instead of using the same volume of solvent for each successive extraction, the solvent-to-waste or soil ratios can be graded in size, as indicated by the extraction volumes pictured in Figure 5. A small solvent-to-solids ratio should probably always be employed for the first extractions. This is usually when the concentration is changing most rapidly, so smaller increments define the curve more accurately. It also is when the soluble species will be the most highly concentrated in the extract and the ionic strength will be at its maximum. Greater dilutions would reduce this, possible affecting the solubility of other components. After the more soluble components have been extracted, the solvent-to-solid ratio can be greatly increased, thus reducing the total number of extractions required. Obviously, the further along the cumulative milliliter per gram axis the extraction volumes extend, the longer the period of column leaching the batch work is equivalent to.

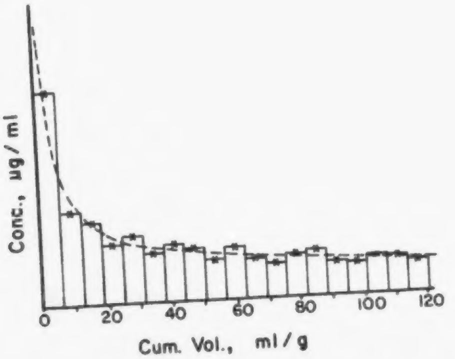

Figure 4. Correlation of Batch with Continuously Leached Columns.

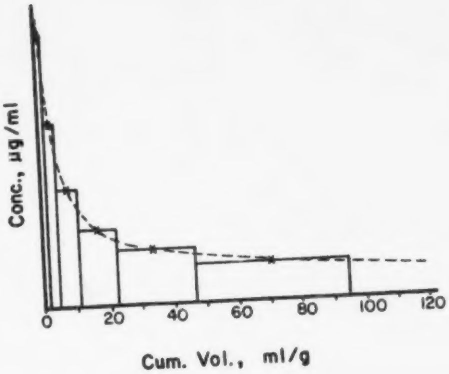

Figure 5. Graded Serial Batch Extractions.

ACCELERATED TESTING

Batch extractions are rapid compared to letting the liquid percolate through a column. If the volume of liquid used in a batch extraction can be related to the same volume of liquid passing through a waste or soil over a period of time, sequential batch extractions can be the basis for an accelerated testing of wastes and soils. The time required for a volume of liquid to penetrate a gram of soil at a selected pore water velocity can be calculated from Equation 1: (7)

$$T = \left(\frac{V}{PV'_g}\right)\left(\frac{1/\rho_b}{v}\right) \qquad (1)$$

where T = time, days,
PV'_g = effective pore volume per gram soil, cm,
ρ_b = soil bulk density, g/cm^3,
v = pore water velocity, cm/day.

This equation was used to prepare Table 1 which applies to the sequence of extraction volumes (the accelerated testing schedule) used in this report. To choose the correct penetration time from the table, the pore water velocity of the liquid in a soil underlying a specific waste-disposal site must be calculated or determined experimentally. (The flowrate-determining factor will often be the penetrability of the layer of waste). This table also applies to the

TABLE 1. CORRELATION BETWEEN EXTRACTION VOLUME AND PENETRATION TIME (7)

Extraction Number	Water Added, (ml/g)	Cumul. Vol., (ml/g)	Equivalent Days of Penetration*		
			@10^{-4} cm/sec	@10^{-5}cm/sec	@10^{-6} cm/sec
1	2	2	0.65	6.5	65.
2	3	5	1.62	16.2	162.
3	6	11	3.56	35.6	356.
4	12	23	7.45	74.5	745. (2.0 yr)
5	24	47	15.2	152.	1520. (4.2 yr)
6	48	95	30.8	308.	3080. (8.4 yr)
7	96	191	61.9	619.(1.7 yr)	6190.(16.9 yr)

*At the specified pore water velocity through a soil having an effective pore volume of 0.223 ml/g.

leaching of waste because the volume of liquid passing through a column of waste will ordinarily be about the same as through the soil beneath it. Similar tables can be calculated for soils having other pore volumes and for other velocities.

TABLE 2. ANALYSES OF SELECTED ELEMENTS IN SECONDARY ZINC SMELTING SLUDGE

Element	Concentration (microgram/gram)
Beryllium	0.82
Boron	57.6
Cadmium	54.5
Chromium	14.8
Copper	1,270.
Lead	68,200.
Magnesium*	920.
Nickel	360.
Zinc	383,000.

*Magnesium was measured in order to correct the lead obtained by argon plasma emission spectrophotometry(7).

MATERIALS AND METHODS

WASTE SAMPLES

Of the industrial wastes which have been examined by this graded serial batch extraction method, data from two wastes of divergent characteristics were chosen to demonstrate here the utility of this procedure for the accelerated testing of wastes and soils, and to show ways the results can be interpreted.

The hydrofluoric acid production waste discussed here is the residue from treating fluorspar with concentrated sulfuric acid. The dry waste is primarily calcium sulfate with a small amount of calcium fluoride and is strongly acid. It contains 4,900 micrograms of fluorine per gram.

The secondary zinc smelter sludge is the residue from the air pollution control scrubber. The amounts of potentially hazardous elements in this waste are shown is Table 2. Their concentrations were followed in each of the waste and soil extracts; the data from cadmium is used in the illustrative example.

WASTE AND SOIL EXTRACTION METHOD

A sequence of seven extracts was made from each waste. Ordinarily a sample of waste was dried to determine moisture content, then sufficient undried sample was weighed to give 300 grams dry weight. (Drying the sample could affect hydrated species and drastically reduce the solubility.) Appropriate volumes of water were added for each extraction to produce the liquid-to-solid ratio given in the second column of Table 3. (If a waste has supernatant water, the volume of the water should be considered as part or all of the first extract.) The sample bottle was shaken gently 4 or 5 times daily (continual mechanical shaking was not used because of concern that it might abrade the waste agglomerates, making them more susceptible to extraction). The time required to reach equilibrium was determined by periodically withdrawing an aliquot for analysis; 24 hours is adequate for most wastes of small particle size. At the end of the extraction period, the mixture was filtered under vacuum using a hardened filter paper (such as Whatman 54) in a Buchner funnel. An aliquot of approximately 20 milliliters of the filtrate was withdrawn for analyzing the ions of interest and filtered through

TABLE 3. SPECIFICATIONS FOR SERIAL BATCH EXTRACTIONS (8)

Extraction Number	Water Added (ml/g)	Volume of Water (ml) Extracting 300 g Waste	Volume of Filtrate Onto a Soil (ml) I 60 g Soil	II 30 g Soil	III 15 g Soil
1	2	600	120	60	30
2	3	900	180	90	45
3	6	1,800	360	180	90
4	12	3,600	720	360	180
5	24	7,200	1,440	720	360
6	48	14,400	2,880	1,440	720
7	96	28,800	5,760	2,880	1,440

a 0.5 μ Millipore filter to remove fine particles which might have by-passed the filter paper and could dissolve when the sample was acidified (after measuring conductance pH, and fluoride ion, one percent concentrated nitric acid was added to the filtrate to inhibit precipitation while standing). The solid waste residue was transferred back to the jar and mixed with the volume of water specified for the next batch. The flow-chart of Figure 6 outlines the sequence of operations.

In the procedure detailed here, the liquid-to-solid ratio was continually increased (Figure 5) to further accelerate the testing,the volume of each extraction after the second one was made double the one before, which redoubles the time represented by that extract.With some wastes, adequate results may be obtainable by using very large volumes right from the first, or, one or two extractions using small liquid-to-solid ratios, followed by a very large one. However, this would have to be checked for each kind of waste by comparison with the more conservative series of extractions utilized in Table 3. Such a procedure would allow rapid simulation of long leaching periods and could be useful in the routine monitoring of variations in waste composition and leachability. (2)

The filtrate resulting from each sequential extraction of the waste was mixed with the first of three batches of each kind of soil. The weights of soil used were 60, 30, 15 grams, representing section I, II, and III, respectively. This gradation in weight allows taking an aliquot of the extract for analysis and having extract left over to challenge the next soil batch at the same liquid-to-solid ratio. Extracting 300 grams of waste yields sufficient solution to challenge three different kinds of soil in experiments set up with the proportions stated in Table 3.

Although the soil equilibrates in six hours or less (9), each solution was kept in contact with the batch of soil before filtration for the same length of time as used to extract the waste. This was to keep the sets of samples progressing smoothly without gaps in the series. After filtering the soil extract, an aliquot was refiltered through a Millipore filter and saved for analysis. The appropriate volume of the remaining filtrate was added to the next batch of soil. The soil exposed to the first waste extract was recovered and mixed with the second waste extract in the series. This was repeated until the waste had been extracted seven times and each waste extract had progressed through all three soil batches. (An eighth extract could have been made to further increase the equivalent leaching time.) This procedure was run in duplicate.

The waste composition changes as components are leached from the waste. Each succeeding portion of extract will therefore generally have a different composition as shown by the upper two histograms of Figure 7. Besides being challenged by a changing solution, the soil's ion-removal characteristics continually change with time as the soil becomes conditioned and loaded by the passage of waste extracts. Since each portion of waste is changed by passage through soil, the conditioning each succeeding segment of soil receives is different and each segment therefore may remove different portions of the various ions present in the waste extract. So although the soil segments start out the same, in effect they become

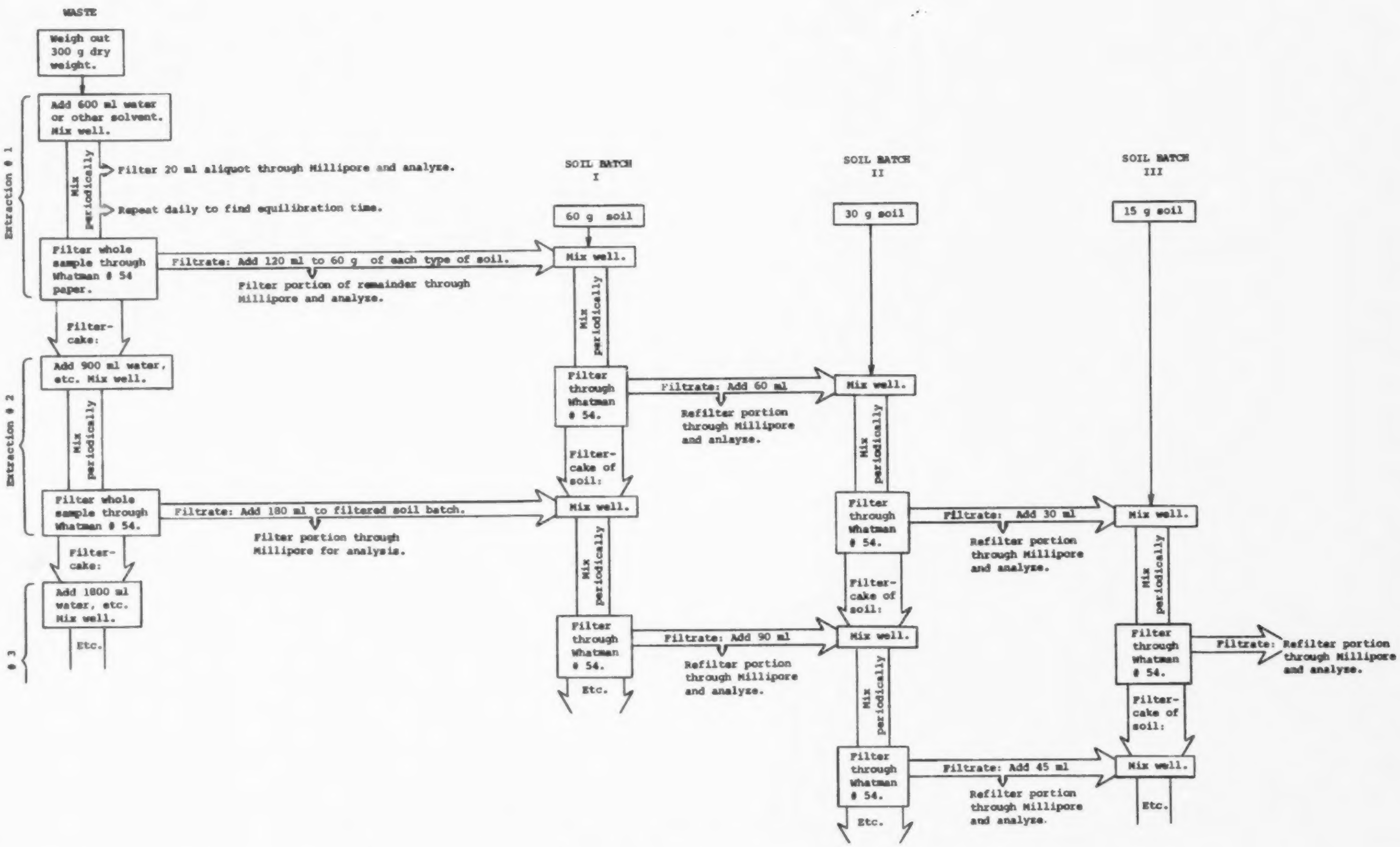
WASTE
Weigh out 300 g dry weight.
Extraction # 1
Add 600 ml water or other solvent. Mix well.
Mix periodically
Filter 20 ml aliquot through Millipore and analyze.
Repeat daily to find equilibration time.
Filter whole sample through Whatman # 54 paper.
Filtrate: Add 120 ml to 60 g of each type of soil.
Filter portion of remainder through Millipore and analyze.
Filter-cake:
Extraction # 2
Add 900 ml water, etc. Mix well.
Mix periodically
Filter whole sample through Whatman # 54.
Filtrate: Add 180 ml to filtered soil batch.
Filter portion through Millipore for analysis.
Filter-cake:
# 3
Add 1800 ml water, etc. Mix well.
Etc.
SOIL BATCH I
60 g soil
Mix well.
Mix periodically
Filter through Whatman # 54.
Filtrate: Add 60 ml
Refilter portion through Millipore and anlayze.
Filter-cake of soil:
Mix well.
Mix periodically
Filter through Whatman # 54.
Filtrate: Add 90 ml
Refilter portion through Millipore and analyze.
Etc.
SOIL BATCH II
30 g soil
Mix well.
Mix periodically
Filter through Whatman # 54.
Filtrate: Add 30 ml
Refilter portion through Millipore and analyze.
Filter-cake of soil:
Mix well.
Mix periodically
Filter through Whatman # 54.
Filtrate: Add 45 ml
Refilter portion through Millipore and analyze.
Etc.
SOIL BATCH III
15 g soil
Mix well.
Mix periodically
Filter through Whatman # 54.
Filtrate: Refilter portion through Millipore and analyze.
Filter-cake of soil:
Mix well.
Etc.

Figure 6. Flow Chart for Graded Serial Batch Extractions.

different soils due to the passage of the different waste extracts.

The soil removes ions from the waste, but the waste extract can also displace ions from the soil. In addition, soil can pick up a specific ion from a waste solution of one composition and then give it up again as the liquid composition changes. The soil may also give up ions later because of intervening conditioning of the soil by the passage of the changing waste extract solution. If extract samples were taken within a layer of soil, it would be possible to study this dynamically-changing situation. This can be accomplished by placing sampling ports in the side of a soil column, as shown in Figure 7. The same results can be attained in a shorter time with far fewer equipment difficulties by putting waste extracts on successive batches of soil and taking a sample after each extraction. A batch of soil then will represent a segment of soil from a soil layer.

Normally, the distribution of substances retained by the soil column is determined after leaching is concluded by sectioning and analyzing the soil column. But this serial batch approach, with sampling between batches of soil allows perceiving what is happening within a bed of soil and provides data which could permit extrapolating to the effect of thicker strata — something which cannot be done with validity from experiments with only a single layer or from experiments which use simpler conditions. It is re-emphasized that batchwise testing also yields its information in a small fraction of the time required by columns or field studies.

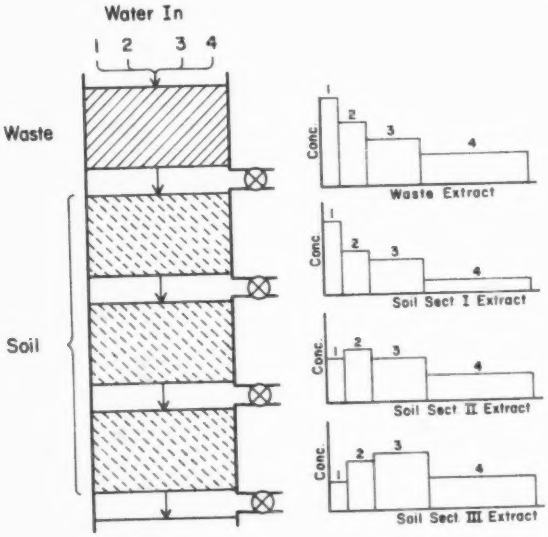

Figure 7. Challenging Multiple Soil Segments with Successive Extracts of Waste.

UTILIZATION OF BATCH EXTRACTION DATA

A variety of calculations can be performed using the results from the graded serial batch extraction experiments on wastes and soils. Table 4 lists those which were done for this report. In Table 4, W refers to the waste extract, and I, II, and III, identify the extraction from the first, second, and third batches of soil, respectively. The subscripts affixed to these symbols identify the number of the extraction in the series of seven employed. The resulting character refers to the amount of a chemical species found in the extract, expressed in terms of micrograms per gram of waste or soil. Each calculation utilizing these quantities is explained in the following paragraphs.

Calculating the Weight of a Substance Leached from Waste

The weight of a substance leached per gram of waste can be calculated by multiplying the concentration of the substance observed in the extract by the volume of water or other extraction liquid used, divided by the weight of waste being extracted. In consistent units: microgram/milliliter x milliliter/gram = microgram/gram waste. Thus, the weight extracted by each extraction in the series listed in Table 3 was obtained by multiplying the observed concentration in micrograms/milliliter by the extraction volumes listed in the second column of the table.

Since one percent concentrated nitric acid was added to keep ions in solution, and ten percent by volume of lithium nitrate solution was added to suppress interference from alkaline metals and earths in the analysis by argon plasma emission spectrophotometer, the observed concentration must by adjusted to obtain the actual concentration. (The correction for the lithium addition was accomplished by programming the concentrations printed out by the spectro-

TABLE 4. CALCULATIONS MADE FROM THE SERIAL BATCH EXTRACTION DATA

A	B	C	D	E	F	G	H	I	J	K	L	M	N
Extraction Number	Layer	Amount Penetrating		Amount Retained this Extract ug/g	Cumulative Total Challenge ug/g	Cumulative Total Retained ug/g	Fraction Retained		Pene-tration Factor	Distribution Coefficients			
		Averaged Raw Data ug/ml	ug/g				From this Extr.	From Cumulative Total Challenge		Including Soil		From Solution Only	
										Distrib. Ratio	Slope, Degrees	Distrib. Ratio	Slope, Degrees
			Out (In)	In-Out	Σ In	Σ(In-Out)	$\frac{\text{In-Out}}{\text{In}}$	$\frac{\Sigma(\text{In-Out})}{\Sigma\ \text{In}}$	$\frac{\text{Out}}{\text{In}}$	$\frac{\Sigma(\text{In-Out})+\text{Soil}}{\text{Out}}$		$\frac{\Sigma(\text{In-Out})}{\text{Out}}$	
1	W	-	W_1	---	---	---	---	---	---	---	---	---	---
	I	-	I_1	W_1-I_1	W_1	W_1-I_1	$\frac{W_1-I_1}{W_1}$	$\frac{W_1-I_1}{W_1}$	$\frac{I_1}{W_1}$	Eqn. 6	Tan^{-1}Eqn. 6	Eqn. 6 with $I_o = 0$	Tan^{-1} ←
	II	-	II_1	I_1-II_1	I_1	I_1-II_1	$\frac{I_1-II_1}{I_1}$	$\frac{I_1-II_1}{I_1}$	$\frac{II_1}{I_1}$	Eqn. 8	Tan^{-1}Eqn. 8	Eqn. 8 with $II_o=0$	Tan^{-1} ←
	III	-	III_1	II_1-III_1	II_1	II_1-III_1	$\frac{II_1-III_1}{II_1}$	$\frac{II_1-III_1}{II_1}$	$\frac{III_1}{II_1}$	Eqn.=8	Tan^{-1}Eqn. =8	Eqn.=8 with $III_o=0$	Tan^{-1} ←
	I+II		$\frac{II_1}{2}$	$\frac{W_1-II_1}{2}$	$\frac{W_1}{2}$	$\frac{W_1-II_1}{2}$	$\frac{W_1-II_1}{W_1}$	$\frac{W_1-II_1}{W_1}$	$\frac{II_1}{W_1}$	Eqn. 9	Tan^{-1}Eqn. 9	Eqn. 9 with I_o, $II_o=0$	Tan^{-1} ←
	I+II+III		$\frac{III_1}{3}$	$\frac{W_1-III_1}{3}$	$\frac{W_1}{3}$	$\frac{W_1-III_1}{3}$	$\frac{W_1-III_1}{W_1}$	$\frac{W_1-III_1}{W_1}$	$\frac{III_1}{W_1}$	Eqn.10	Tan^{-1}Eqn. 10	Eqn.10 with I_o, II_o, III_o $=0$	Tan^{-1} ←
2	W	-	W_2	---	---	---	---	---	---	---	---	---	---
	I	-	I_2	W_2-I_2	W_1+W_2	$(W_1-I_1)+(W_2-I_2)$	$\frac{W_2-I_2}{W_2}$	$\frac{(W_1-I_1)+(W_2-I_2)}{W_1+W_2}$	$\frac{I_2}{W_2}$	APPLY ABOVE EQUATIONS			
	II	-	II_2	I_2-II_2	I_1+I_2	$(I_1-II_1)+(I_2-II_2)$	$\frac{I_2-II_2}{I_2}$	$\frac{(I_1-II_1)+(I_2-II_2)}{I_1+I_2}$	$\frac{II_2}{I_2}$				
	III	-	III_2	II_2-III_2	II_2+II_2	$(II_1-III_1)+(II_2-III_2)$	$\frac{II_2-III_2}{II_2}$	$\frac{(II_1-III_1)+(II_2-III_2)}{II_1+II_2}$	$\frac{III_2}{II_2}$				
	I+II		$\frac{II_2}{2}$	$\frac{W_2-II_2}{2}$	$\frac{W_1+W_2}{2}$	$\frac{(W_1-II_1)+(W_2-II_2)}{2}$	$\frac{W_2-II_2}{W_2}$	$\frac{(W_1-II_1)+(W_2-II_2)}{W_1+W_2}$	$\frac{II_2}{W_2}$				
	I+II+III		$\frac{III_2}{3}$	$\frac{W_2-III_2}{3}$	$\frac{W_1+W_2}{3}$	$\frac{(W_1-III_1)+(W_2-III_2)}{3}$	$\frac{W_2-III_2}{W_2}$	$\frac{(W_1-III_1)+(W_2-III_2)}{W_1+W_2}$	$\frac{III_2}{W_2}$				

photometer.) The corrected raw data from replicate extractions is averaged and posted as column C, Table 4, Multiplying each waste-sample concentration by the appropriate above-mentioned factor yields the corresponding result in column D.

Calculating the Weight of a Substance Penetrating and Retained on Soil

The weight of a substance extracted per gram of soil is calculated for each extraction in the same manner as described above for waste. The multiplying factors remain the same because the extraction volumes in Table 3 were adjusted for all the soil batches to maintain the same milliliter/gram as for the waste.

The amount penetrating a batch of waste or soil becomes the challenge to the next batch. Thus, the μg/g out of the W_1 becomes the μg/g in for I_1. The weight of a substance coming in to a batch of soil minus the weight out equals the weight retained by the soil during the extraction. In this way, the values entered in column D, Table 4 are used to produce column E. The fraction retained by a soil from an extract is calculated by dividing the results in column E by the weight coming in, as indicated in column H.

Whenever a calculated value has a minus sign, it means that the soil either gave up some of that substance which it had previously picked up from the waste leachate, or it gave up some originally present in the soil before being exposed to that waste. If the original analyzed concentrations were near the detection limit, then, because of the normal deterioration of the precision of an assay near its detection limit, less significance can be assigned to the corresponding derived values and to the appearance of a minus sign.

A useful property of the fraction retained from the cumulative total challenge is that when the soil is yielding the element of interest and it is desired to know how many time greater the amount exiting is greater than the challenge, change the minus sign on the value in column I to a plus and add 1.00. Thus, a fraction of -8.05 retained from the total challenge means that 9.05 times as much of that element was given up as was present in the total challenge.

The results of passing one waste extract through the three soil batches can be presented as in the histogram of Figure 8. The height of the histogram bar labeled W represents the mass in micrograms of a substance extracted per gram of waste. This is the challenge to the first batch of soil, which represents the top layer in a bed of soil. The height of the bar labeled I shows the concentration of the species penetrating the batch representing the next layer of soil, and the difference in height between I and W is the amount of the species retained per gram of soil.

The cumulative sum of the challenges to a given batch (layer) of soil is obtained by summing up the results for the successive extractions that have challenged that batch. Thus, as seen in column F of Table 4, the cumulative sum of the challenge to soil II_2 is $I_1 + I_2$. The cumulative total retained can be calculated in a similar manner, as indicated in column G, and used to determine the fraction retained from the total challenges, as recorded in column I. These values are of particular interest in studies of soil capacity.

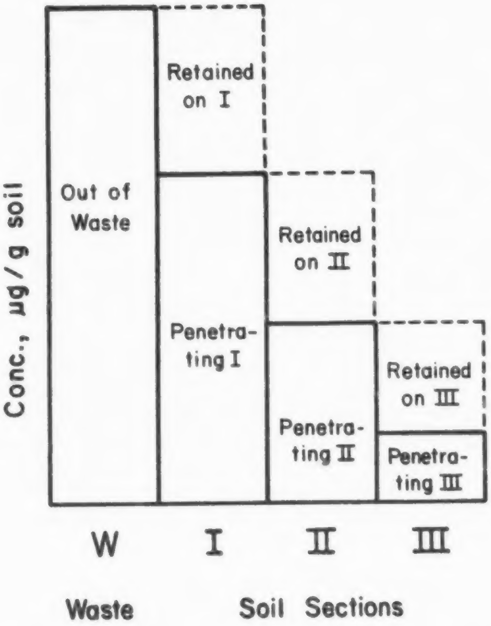

Figure 8. Histogram Showing the Penetration and Retention of a Species by Soil for One Set of Extractions.

Calculating Penetration Factors

The quantity of a substance penetrating a batch of soil divided by the amount of challenge (both found in column D) can be defined as the Penetration Factor (the reciprocal of the Attenuation Factor), which is found in column J of Table 4. This is the fraction penetrating the soil and it can also be viewed as the decimal percent. Multiplying a challenge by the Penetration Factor gives the amount penetrating. If the Penetration Factor is greater than 1.0, it indicates that the soil is either yielding material previously held up during the passage of extracts, or that some is being displaced out of that originally present in the soil.

The penetration factor calculated in column J is for the corresponding extraction only and is not cumulative. The cumulative penetration factor can be obtained by subtracting the cumulative fraction retained, column I, from 1.00.

Calculating Distribution Coefficients(10)

The chromatographic distribution coefficient, K, is defined as the concentration of a species in the solid phase divided by the concentration in the liquid phase. (11) This distribution ratio (columns K and M of Table 4) is the slope of the line showing the relationship between the concentration adsorbed on the soil and the concentration remaining in the solution. The angle of the slope at the point is the arctangent of K. (The angles are tabulated in column L and N.) At low concentrations, the relationship is usually linear in simple systems, but K typically decreases with increasing amounts of solute, i.e., as the sites are occupied by increased amounts of the substance being studied. Large K's show a high relative retention. Experiments to determine K are normally done at constant temperature because K is temperature dependent (changing the temperature changes the position of a point on the plot showing the amount of a species removed from the solution by the soil) and so the curves are called isotherms.

Temperature is not the only parameter which affects the distribution between phases. The pH, the ionic strength, the presence of competing ions, the previous history of the solid, its current surface energy and effective surface area, in short, the total conditions must be uniform because each of these things can affect the distribution ratio. So, iso-conditons are needed, not just iso-therm, while experiments are run if this kind of plot is to be obtained. If the conditions are changed to some other level, a distinctly different set of points can be obtained. (If conditions are allowed to vary at random, then randomly located points can be expected; if conditions are varied according to some plan, like a factorial experiment design, then their effect on the distribution coefficient can be examined. For the results to apply to a field situation, field conditions must be simulated in the experimental array.)

These lines are called adsorption isotherms, but more than adsorption can be involved in removing ions from solution. Besides dispersion and dipole forces, hydrogen bonds and weak covalent bonds, acid-base interactions and complex formation, strong covalent bonding responsible for chemisorption, precipitation, and even mechanical filtration, all could contribute to the removal of a substance from solution. So what are called adsorption isotherms really are plots of removal or retention in iso-conditions, that is, they are plots of temporary retention under a given set of conditions. Even irreversibility is condition-dependent. An insoluble compound may become soluble as the conditions change, e.g., as the extraction progresses or as the soil changes.

The distribution coefficient, K, is not for adsorption alone, but for all equilibria causing retention or displacement. K can be computed on several different bases; as an experiment is started, the concentration of a substance being studied will probably be zero in the solid phase if a chromatographic substrate is being worked with, but in soil work, any compounds present in the soil which contain the ion(s) being studied are a potential source that can contribute to its concentration in the leachate solution passing through the soil. The waste leachate is a potentially powerful solubilizer and displacer of components in the soil, i.e., the soil can act as a reservoir of Pb, Cd, Ti, Zn, etc., which the waste leachate can cause to bleed off and carry on down to ground-water. A negative slope to the retention isotherm shows the soil is giving up the ion, acting as a source. The waste is the cause of this kind of pollution, but not the source—the soil is the source.

The distribution coefficient, K, can be based on a unit volume of solid adsorbant, or a unit weight, which is employed in this report. The concentration expressed in microgram/gram soil can refer to the number of micrograms of ion removed from a given solution challenging the soil, it can represent all that the soil has removed from a series of solutions (as in column M of Table 4), it can be a total which also includes all that was originally present in the soil and therefore potentially available to the equilibria (as used in column K), or the total concentration in the soil can include just that portion known to be soluble in or displaced by the solution challenging it.

The concentration in the solution is usually expressed as weight per unit volume, such as micrograms per milliliter, and the resulting units for K are milliliters per gram, as shown in equation (2):

$$K = \frac{\mu g/g}{\mu g/ml} = \mu g/g \times ml/\mu g = ml/g. \quad (2)$$

But, even though it is the liquid that is being analyzed, it is the soil that is being studied. The concentration is measured as micrograms per milliliter, but of more direct importance is the weight of soil contacted by this solution. If the concentration observed in the liquid, micrograms/milliliter, is multiplied times the total amount of liquid put on the soil, expressed as milliliters/gram, Equation (3) shows that the concentration in the solution is obtained in terms of micrograms per gram of soil contacted.

$$\mu g/ml \times ml/g = \mu g/g. \quad (3)$$

Then, as seen in Equation (4) the ratio, K, becomes a properly dimensionless constant as a result of employing this more fundamental relationship:

$$K = \frac{\mu g/g}{(\mu g/ml)\ (ml/g)} = \frac{\mu g/g}{\mu g/g} \quad (4)$$

As previously, discussed, the conditions for retention can be expected to differ with soil depths because each layer of soil is challenged by a different solution matrix. The conditions also will change with time as the leaching of the waste progresses and generates a solution of changing composition. So that this latter effect could be examined, equations were derived to calculate the distribution coefficient for every succeeding extraction of the waste. The distribution of a species between the solid and the liquid phases will be the sum of the amount originally on the soil and the amounts retained from each of the successive waste extracts, all divided by the amount in the solution leaving that batch of soil. Thus, the distribution ratio resulting from n extracts passing through soil batch I can be computed by the following equation:

$$K_{I_n} = \frac{I_o + (W_1 - I_1) + (W_2 - I_2) + \dots (W_n - I_n)}{I_n} \quad (5)$$

$$= \frac{I_o + \sum_{i=1}^{n} (W_i - I_i)}{I_n} = \text{Slope of adsorption isotherm,} \quad (6)$$

where,

I_o = concentration of a species originally on the soil, µg/g,

I_i = concentration of the species in the *i*th extract passing through soil batch I, µg/g, and,

W_i = concentration of the species in the *i*th extract out of the waste, µg/g.

The concentrations of the solutions after equilibrium has been established (the output concentrations) are used in these calculations instead of the starting (the input) concentrations.

The distribution ratio will ordinarily be different for the second batch of soil because it is being challenged and conditioned by a different solution — a solution which has been modified by passing through the first batch of soil. The distribution coefficient for the second soil batch can be calculated for each extraction using the following formula:

$$K_{II_n} = \frac{II_o + (I_1 - II_1) + (I_2 - II_2) + \dots (I_n - II_n)}{II_n} \quad (7)$$

$$= \frac{II_o + \sum_{i=1}^{n} (I_i - II_i)}{II_n} = \text{Slope.} \quad (8)$$

The distribution coefficients for each extraction passing through the third batch of soil are calculated in a similar manner using the differences in concentration between the second and third soil batches.

The experiments generally will be done with the same kind of soil in each batch, so the concentration of a species originally in the batch of soil, $I_0 = II_0 = III_0$. If only the amount of a species removed from the solution is to be considered in the distribution coefficients being calculated, neglecting that which is originally present in the soil, set I_0, II_0, and III_0 all equal to zero.

The effect of different soil-to-waste ratios can also be checked in this experiment by calculating distribution coefficients for the waste extract challenging the first two soil batches and then all three batches:

$$K_{(I+II)_n} = \frac{I_0 + II_0 + \sum_{i=1}^{n} \frac{(W_i - II_i)}{2}}{1/2 \; II_n} \quad . \qquad (9)$$

for a 2:1 soil-to-waste ratio, and

$$K_{(I+II+III)_n} = \frac{I_0 + II_0 + III_0 + \sum_{i=1}^{n} \frac{(W_i - III_i)}{3}}{1/3 \; III_n} \qquad (10)$$

for a 3:1 soil-to-waste ratio.

The effect of changes in the extract due to passage through the soil also can be obtained by calculating:

$$K_{(II+III)_n} = \frac{II_0 + III_0 + \sum_{i=1}^{n} \frac{(I_i - III_i)}{2}}{1/2 \; III_n} \quad . \qquad (11)$$

and comparing it with the results from $K_{(I+II)n}$ (Equation 9).

Since a distribution coefficient is the slope of the retention curve (the "isotherm") at the point represented by the numerical values of the numerator and denominator in the ratio, the angle whose tangent is K can be depicted on a graph by an appropriately oriented line segment. This seemingly would allow drawing a curve of retention under iso-conditions (an "isotherm"). But an examination of the experimental data reveals, as postulated when designing this experimental approach, that there is a considerable change in K for most ions as the leaching of the waste progresses and as the waste passes down through the soil. This shows that in the real field situation, or in experiments which approximate it, constant conditions for adsorption will not exist during the presentation of the challenge. This means that the remainder of the curve cannot be determined. Only a family of line segments will be obtained from the K values calculated for each waste and soil extract, with each line segment representing the distribution ratio under a different set of conditions. (An example is depicted in Figure 13, back where the data are discussed.)

INTERPRETATION OF RESULTS FROM INDUSTRIAL WASTE EXTRACTION

The samples of wates were collected from a hydrofluoric acid manufacturing plant, and a zinc secondary-refining operation. These wastes were examined for the water-extractibility of certain inorganic ions during a series of seven extractions. The resulting leachates were then applied, in sequence, to three batches (corresponding to three layers) of each of three different clay soils. The data for Chalmers soil is used here to demonstrate the interpretation of results. Analysis of the solutions for pH, conductivity, and concentrations of specified ions before and after contact with the soils allowed observing the effect of a soil on the leachate, as well as seeing how later changes in the leachate affected the retention of an element on a soil. No attempt was made to investigate the mechanisms responsible for the soil and waste leachate interactions.

The wastes discussed as examples represent a reasonably wide range of waste characteristics from very soluble to relatively insoluble, and from extremely acidic to near neutral. These practical applications provided data which could be presented in a variety of ways.

First, a short table is used to indicate the leachability of the element of interest in from a waste. (Tables 5 and 6 are examples.)

TABLE 5. LEACHABILITY OF HYDROFLUORIC ACID PRODUCTION WASTE

Element	Initial Conc. (µg/ml)	When Concentration Levels Off Conc. (µg/ml)	Extr. Nr.	Extr.Vol. (ml/g)	Equiv. Days	Total Weight Extracted (µg/g waste)	Percentage Extracted
F	970.	2.4	7	190	620	2,760.	56.

Measurement	Initial	Final	Estim.Tot. Extr. (µ equiv/g)
Conduct. (µ mho)	33,300.	1786.	4480.
pH	2.2	3.7	

TABLE 6. LEACHABILITY OF SECONDARY ZINC SMELTER SLUDGE

Element	Initial Conc. (µg/ml)	When Concentration Levels Off Conc. (µg/ml)	Extr. Nr.	Extr. Vol. (ml/g)	Equiv. Days	Total Weight Extracted (µg/g waste)	Percentage Extracted
Cd	116.	0.08	7	190	620	410.	75.
Pb	9.5	7.5	7	190	620	1,540	2.2
Ni	0.66	0.6	5	47	150	5	1.4
Zn	605.	21.	7	190	620	11,600	3.0

Measurement	Initial	Final	Estim.Tot.Extr. (µ equiv/g)
Conduct. (µ mho)	9,524.	148.	886.
pH	6.4	6.0	

The column labeled Initial Concentration refers to the concentration in the first extract. Next, the point in the series of extractions when the concentration in the extract levels off is identified. The equivalent leaching time is taken from Table 4 and is offered as a comparative index of the rate of leaching. The next column in the table gives the total weight of the element extracted per gram of waste. This is calculated up through the extraction prior to the one in which the lower detection limit (LDL) was reached or up through the seventh extraction if samples remained above the LDL. The last column in the table gives the percentage this weight represents of the total weight of an element in the waste.

The bottom portion of these waste leachability tables gives the conductance and pH in the first and seventh waste extracts. The specific conductance was measured for each sample because it is a convenient indicator of the solubilization of materials from a waste or soil. Multiplying the specific conductance by 0.01 yields an estimate of the number of microequivalents of dissolved solids per milliliter for many waters (12). Multiplying the microequivalents/milliliter by the sample volume gives the total microequivalents of dissolved ionic species present in the extract. The figure given in the table is the cumulative sum calculated from all seven extracts. Although its accuracy will vary depending upon the equivalent conductances of the mixture of ions present in the solution, this figure provides an estimate of the amount of waste that dissolved.

For each element of interest a graph was prepared showing its leachability from the waste. (See for example Figures 9 and

10.) The y-axis gives the concentration, micrograms/milliliter, of the element found in the extract. The cumulative volume scale on the x-axis is accompanied by a scale giving the calculated correlation with time, showing the equivalent number of years of exposure to a source of water which is moving through the waste into the underlying soil at a pore water velocity of 1 x 10-5 cm/sec. The lower detection limit for the assay is indicated to the far right for guidance in evaluating the significance of the histogram bar height. Above the histogram bar is printed the total weight of the element liberated by that extraction. This is expressed as micrograms per gram of waste, which is equivalent to grams per metric ton of 2204.6 pounds. If and when the lower detection limit is reached, no weight is given because the result in this region are undefined: they can be anywhere in the range from zero to the weight calculated from the detection limit.

Each waste characterization histogram is followed by a set of histograms (one for each extraction) which compares the fraction of that element retained from the waste leachate by the three soils for three different soil-to-waste ratios (1:1, 2:1, and 3:1). The height of the histogram bar and the value printed on it show the fraction retained from the cumulative total challenge up to the point represented by that extraction (calculated as in column I, Table 4). If the soil gives up that element then the negative value is printed under the space corresponding to the appropriate layer of soil. The soils tested are designated by the letter C for Chalmers, D for Davidson, and N for Nicholson soil.

For example, the results of taking the leachate from the extraction of zinc secondary refining sludge, and challenging the soil batches are given in Figure 11.

The first bar in the first histogram of extract 1 (EXTR.1) shows that 54 percent of the cadmium present in the first extract had been retained by Chalmers soil at a 1:1 soil-to-waste ratio. When this resulting solution was placed on the second batch of soil, a total of 86 percent of the cadmium was removed by passage through what is now a 2:1 soil-to-waste ratio. The solution from the second batch was placed on the third batch of soil. A total of 97 percent of cadmium was retained after passage through what is now a 3:1 soil-to-waste ratio. As the extraction proceeded and the soil batches were placed in contact with the subsequent waste extracts, less and less of the total cadmium extracted from the waste was retained by the soil. By the seventh extract not only had all the cadmium previously retained by the first soil batch at 1:1 been released but some of the cadmium normally present in the soil also had been released, as shown by the -6 percent. Even the second and third soil batches released significant quantities of the previously-retained Cadmium by the seventh extract, and could conceviably have released all of it if the leaching had proceeded further or if a different waste extract was then used to challenge the soils to simulate co-disposal.

The histograms of Figure 11 provide a direct comparison of the ability of three soils to attenuate one ion from the particular waste as the leaching proceeded. The soil's behavior toward that ion would be expected to be different if the ion were present in a waste of different composition. A soil modified by prior exposure to waste of the same or different composition would also behave differently.

In addition to the above-mentioned waste characterization curves and the summarizing soil-retention histogram, a series of tables and graphs were prepared that detail, for each kind of soil, the results obtained for each element extracted from a waste. A table of values calculated from the batch extraction data in the manner shown in Table 8, was printed out for each soil. From this data, sets of histograms can be prepared that give the weight, micrograms per gram waste or soil, of element observed in the extracts from the waste (designated by histogram bar W) and from each batch of soil (I, II, III) for each of the seven extractions. This latter histogram thus shows the amount of element penetrating or released from the soil. Figure 12 is an example showing cadmium leached from zinc secondary-refining sludge and passing through Chalmers soil. The analytical detection limits are indicated to the right of this type of histogram, but here the position of the arrow specifies micrograms of the ion per gram of waste or soil to be consistent with the units on the histogram. (The liquid-to-solid ratio was kept the same for W, I, II, and III so that results could be expressed as micrograms per gram of either waste or soil.) Because

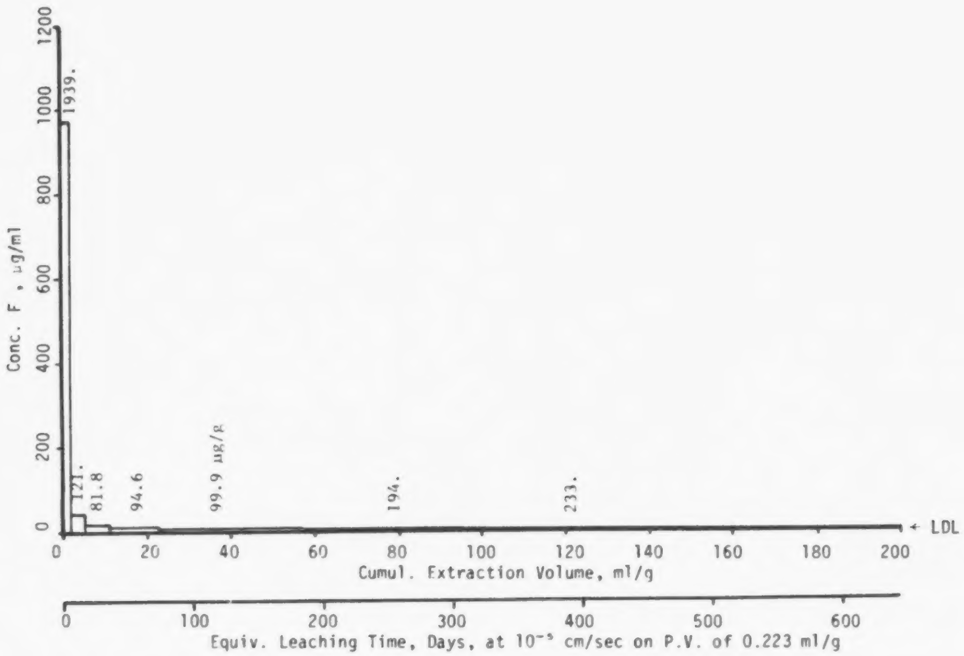

Figure 9. Extraction of Fluorine from Hydrofluoric Acid Production Waste.

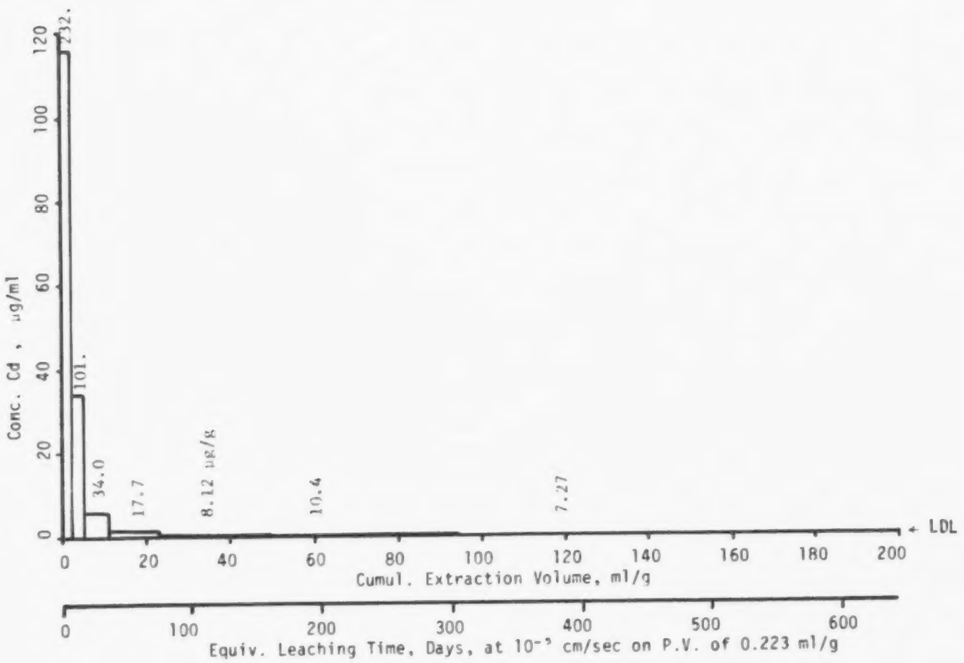

Figure 10. Extraction of Cadmium from Zinc Secondary-Refining Sludge.

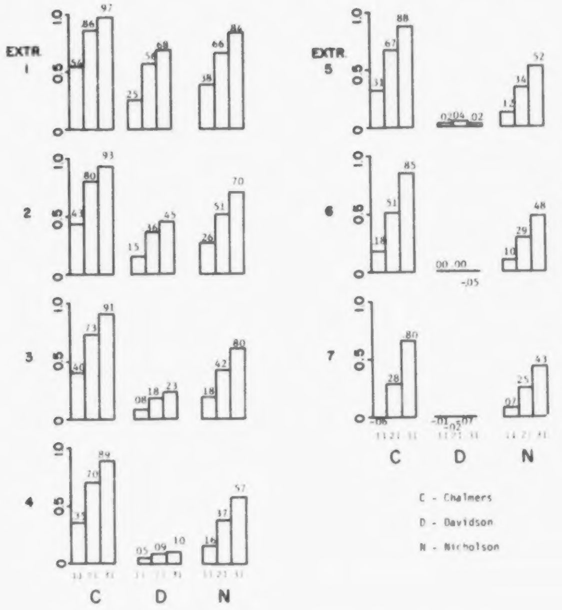

Figure 11. Comparing Fraction Cadmium Retained by Soils from Zinc Secondary-Refining Sludge Leachate.

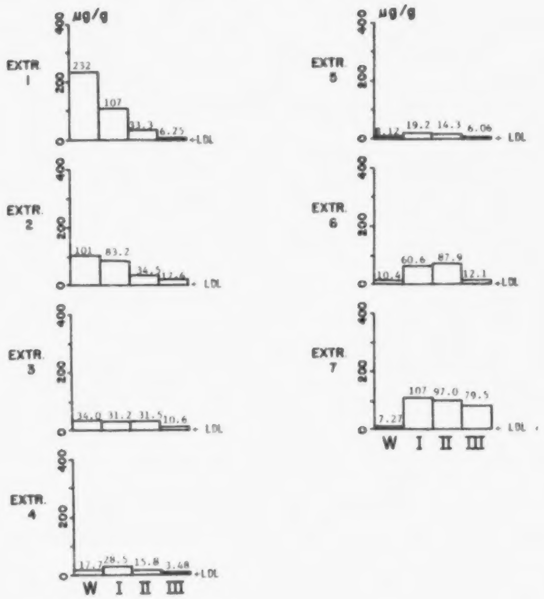

Figure 12. Weight of Cadmium from Zinc Secondary-Refining Sludge on Chalmers Soil.

the detection limits are given as a weight of element per weight of waste or soil, they increase with each succeeding extraction, because increasing volumes of solution are used to extract a fixed weight of waste or soil. This is not apparent in Figure 12 because of the scale required to depict the high concentration of cadmium.) For this reason the histogram bar height will increase as the extraction proceeds, for the case when the output concentration becomes constant, because a given concentration in a larger volume represents a greater weight. So it is necessary to note that these soil histograms are expressed in terms of weight of element per unit weight of waste or soil. (The corresponding concentrations in micrograms per milliliter can be obtained from the accompanying tables.) The histogram identified as EXTR.1 in Figure 12 shows that the 1st time the sample of zinc secondary-refining cludge was extracted, the solution from W contained 232 micrograms cadmium per gram of waste. This solution was mixed with the first batch (I) of soil. (A flowchart of the serial batch extraction procedure is shown in Figure 6 for the first two extractions.) When the solution was filtered, it contained 107. micrograms cadmium per gram of soil contacted by the solution; the difference between W and I had been retained by the soil. The solution filtered from soil batch I was mixed with soil batch II for a predetermined length of time. After filtering II, analysis of the filtrate showed that soil batch II had reduced the solution concentration to 33.3 micrograms cadmium per gram of soil contacted. This corresponds to the concentration penetrating a second layer of soil. The difference, 107 minus 33.3 or 74 micrograms cadmium per gram, was retained by the soil. The solution from II was mixed with soil batch III and the solution concentration of the resulting filtrate was 6.25 micrograms cadmium per gram. Of the initial 232. micrograms cadmium per gram in the first extract, only 6.25 micrograms cadmium per gram penetrated (i.e., was not retained by) the three soil batches. The weight of waste and soil were chosen so that this corresponds to the penetration through the amount of soil equivalent to a 3:1 soil-to-waste ratio.

Although analytical variations will be responsible for some of the differences within sequences, the progressing waste extraction and the passage of the resulting solution through the soil continually changes the environment and the soil. Thus, what

TABLE 7. CADMIUM FROM ZINC SECONDARY-REFINING SLUDGE ON CHALMERS SOIL.

EXT.		AMT.PENETR.		AMT.RETD. THIS EXT.	CUM.TOT. CHALLG.	CUM.TOT. RETD.	FRACTION RETD.		PENETR.	DISTRIBUTION COEFFICIENTS			
							THIS	TOTAL		INCL SOIL		SOLN ONLY	
NR.	LAYER	µG/ML	UG/G	µG/G	µG/G	µG/G	EXTR.	CHALLG.	FACTOR	RATIO	DEG.	RATIO	DEG.
1	W	115.90	231.79										
	I	53.68	107.36	124.43	231.79	124.43	.54	.54	.46	1.16	49.33	1.16	49.21
	II	16.67	33.33	74.03	107.36	74.03	.69	.69	.31	2.24	65.91	2.22	65.76
	III	3.13	6.26	27.07	33.33	27.07	.81	.81	.19	4.40	77.20	4.32	76.97
	I+II			99.23	115.90	99.23	.86	.86	.14	6.01	80.56	5.95	80.47
	I+II+III			75.18	77.26	75.18	.97	.97	.03	36.73	88.44	36.02	88.41
2	W	33.71	101.13										
	I	27.72	83.17	17.95	332.92	142.38	.18	.43	.82	1.72	59.80	1.71	59.71
	II	11.51	34.54	48.63	190.54	122.66	.58	.64	.42	3.57	74.33	3.55	74.27
	III	5.86	17.57	16.97	67.87	44.04	.49	.65	.51	2.53	68.47	2.51	68.24
	I+II			33.29	166.46	132.52	.66	.80	.34	7.73	82.63	7.67	82.57
	I+II+III			27.85	110.97	103.03	.83	.93	.17	17.84	86.79	17.59	86.75
3	W	5.67	34.03										
	I	5.20	31.21	2.82	366.95	145.20	.08	.40	.92	4.67	77.91	4.65	77.87
	II	5.25	31.51	-.30	221.75	122.36	-.01	.55	1.01	3.90	75.61	3.88	75.56
	III	1.77	10.60	20.91	99.38	64.94	.66	.65	.34	6.17	80.80	6.12	80.73
	I+II			1.26	183.47	133.78	.07	.73	.93	8.55	83.33	8.49	83.28
	I+II+III			7.81	122.32	110.84	.69	.91	.31	31.78	88.20	31.35	88.17
4	W	1.47	17.70										
	I	2.37	28.48	-10.79	384.64	134.42	-.61	.35	1.61	4.74	78.08	4.72	78.04
	II	1.31	15.76	12.73	250.23	135.09	.45	.54	.55	8.61	83.37	8.57	83.35
	III	.71	8.48	7.27	115.14	72.22	.46	.63	.54	8.57	83.35	8.51	83.30
	I+II			.97	192.32	134.75	.11	.70	.89	17.23	86.68	17.10	86.65
	I+II+III			3.07	128.21	113.91	.52	.89	.48	40.91	88.60	40.29	88.58
5	W	.34	8.12										
	I	.80	19.15	-11.03	392.76	123.39	-1.36	.31	2.36	6.47	81.21	6.44	81.18
	II	.60	14.30	4.85	269.38	139.94	.25	.52	.75	9.82	84.19	9.78	84.16
	III	.25	6.06	8.24	129.44	90.46	.58	.62	.42	13.36	85.72	13.29	85.69
	I+II			-3.09	196.38	131.66	-.76	.67	1.76	18.55	86.91	18.41	86.89
	I+II+III			.69	130.92	114.59	.25	.88	.75	57.47	89.00	56.73	88.99
6	W	.22	10.42										
	I	1.26	60.60	-50.19	403.19	73.21	-4.81	.18	5.81	1.22	50.57	1.21	50.38
	II	1.41	67.87	-7.27	329.98	132.66	-.12	.40	1.12	1.96	62.99	1.95	62.91
	III	.25	12.12	55.75	197.31	136.21	.82	.69	.18	11.29	84.93	11.24	84.92
	I+II			-28.72	201.59	102.94	-5.51	.51	6.51	3.06	71.92	3.03	71.75
	I+II+III			-.57	134.40	114.03	-.16	.85	1.16	28.60	88.00	28.22	87.97
7	W	.08	7.27										
	I	1.11	106.66	-99.38	410.46	-26.17	-13.67	-.06	14.67	-.24	-13.53	-.25	-13.79
	II	1.01	96.96	9.70	436.63	142.36	.09	.33	.91	1.47	55.83	1.47	55.74
	III	.83	79.51	17.45	294.27	153.66	.18	.52	.82	1.94	62.72	1.93	62.64
	I+II			-44.84	205.23	58.09	-12.33	.28	13.33	1.22	50.63	1.20	50.15
	I+II+III			-24.08	136.82	89.95	-9.93	.66	10.93	3.45	73.84	3.39	73.58

happens in one batch is not necessarily an indication of what to expect in the next. (This unpredictability is expressed by the varying concentrations and changing slopes of the isotherm segments shown in Figure 13.) In many cases a chromographic type "peak" can be clearly seen to move though soil batches I, II, and III. In other cases the peak remains "submerged" and is discernable only as a wave of lowered retention progressing through the soil as the extractions are continued.

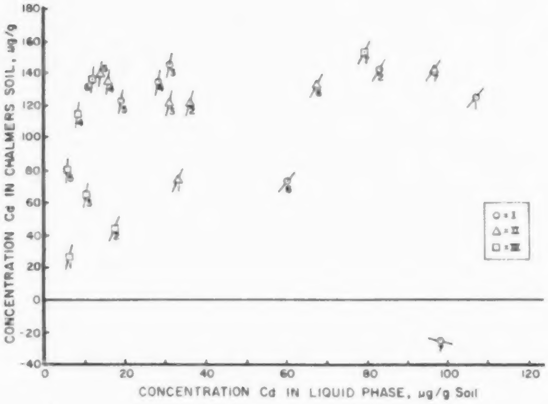

Figure 13. Segments of Adsorption "Isotherms" Showing the Effects of Soil Depth (Layers I to III) and Extent of Leaching (Extractions 1 to 7) on Cadmium Distribution.

CONCLUSIONS

If the interest in obtaining equations which describe a complex system is not for theoretical purposes but is for practical applications like predicting a response resulting from known levels of given variables, then obtaining purely empirical equations should be a more straight-forward approach. But caution is still required if the equations are to describe a field situation. Equation parameters should be derived from experiments that include all of the factors having significant effects. The design of the experiment should be such that the scope of its applicability and its relation to an actual field situation will minimize the number of assumptions needed in the corresponding prediction equations. This will improve the validity of the predictions. For example, the changes in K show that the experiments should employ an actual changing waste leachate so that predictions will not have to be based on the assumption of a constant composition or so that the nature of the changes will not have to be assumed. The closer the laboratory simulation approaches a field situation, the fewer additional assumptions that will have to be applied and the more reliable the predictions likely will be. Rapid experimentation which is flexible enough to simulate each new field situation even makes case-by-case experimental determinations practical, thus reducing to a minimum the dependence upon the ability of an equation to extrapolate.

Except for helping to identify potential experimental factors, it is our opinion that mathematical models should not be introduced too soon in an attempt to construct an expression meant to predict the behavior of a complex physical-chemical system. Experimental examination of the effects of impressed variations can (if the experiments are suitably designed) take into account the effect of unidentified (unknown) factors. Afterward, in the application of these results, mathematical compensation may be introduced to correct for those factors which were not included in the experimental set-up (such as upward capillary flow, horizontal spreading, etc). Additional experimentation may be required to quantitate these effects. The final description of the predictions should be in a mathematical framwork which yields output weight or concentration in terms of time, volume, etc., upon plugging in values for all factors which differ from those employed in the experimental determinations or those effects which otherwise need correction (like experiments on a saturated system being applied to predictions on unsaturated soil).

In this connection, some comments are in order concerning the nature of the proposed graded serial batch extraction procedures:

a. Batch extractions have been considered to be of zero dimensionality. (13) The batch extraction method is independent of soil dimension in one sense, but the relation employed in the design of the experiments reported here yields results expressed per unit volume of soil, i.e., in three-dimensional space. In the application of these results to the field, the effect of horizontal spreading (how the space occupied by the volume changes with time) can be taken into account.

b. Even though an extraction can be classified as static with respect to liquid-front movement, the sequential extractions proposed here simulate a stepped dynamic situation so a steady state need not be assumed for prediction equations in which these data are applied. The proposed batch extraction experiments thus should provide very useful input data for a variety of transport models. (Predictions are better based on laboratory simulations than upon completely mathematical "simulations".) Additional soil batches (i.e., more than three) could be used to better define what happens with increasing penetration depth into the soil.

c. The serial batch experiments provide direct information for saturated-only transport models. Corrections must be inserted if there is a significant difference caused by unsaturation. (Comparison between batch and column showed no difference for most ions studied.) (2) The rate of movement could also differ greatly without causing significantly different adsorption equilibria, i.e., the K values may be sufficiently alike so long as equilibrium is attained.

d. The calculated time equivalencies listed in Table 1 are for the idealized case of a uniformly-packed bed of soil (similar to that prepared in a column or for a lagoon lining). Inhomogenities in composition (such as steaks of sand in a bed of clay) or fissures produced by, e.g., rotten roots, will not only greatly increase the liquid front velocity in those zones but the resulting channeling can significantly reduce the effective mass of soil contacted by the waste extract. For example, if channeling is bad, 70 percent of the liquid may leak through and contact but a small fraction of the soil, while only the remaining 30 percent of the waste leachate would be available to percolate through the bulk of the soil. Corrections can be readily included for this kind of deviation from ideality if their relative magnitudes can be estimated for the site of interest. Another situation that would affect the liquid-front velocity presumed for a given bed of soil, one which would require separate flow-rate column to detect, is the case where the waste leachate itself affects the flow through the soil, either by plugging the pores and reducing the flow, or by affecting the soil structure and drastically increasing the flow-rate (this was observed with flue gas waste on Davidson soil (14)).

e. It is recognized that in the field very slow processes may contribute to the net retention or even change the conditions under which retention is occurring (like micro-biological modification of the leachates and/or soils). The relative net effect of the slow to the fast processes during the time of contact will determine their significance. If slow processes have a significant proportional effect, it may not be possible to accelerate the testing by reducing the contact time below the residence time calculated for a given liquid front velocity. However, it is also not desirable simply to wait for equilibrium to be established if this requires longer than the field residence time for a slug of liquid of a given composition.

A change in the distribution coefficient shows a shift in the equilibrium. The change in K could be plotted versus pH or hydrogen ion concentration, the concentration of other ions, or against the measured values observed or calculated for the slope, or other responses of concern could be regressed against the level of selected experimental factors to see if a simple relation exists between a response and a factor. (i.e., test for or derive a relationship between the measured or calculated parameters and the experimental variables.) But, it is necessary to be careful when drawing conclusions in this way. What is being done with the data to relate factors (variables) may be analogous to classical vary-one-factor-at-a-time experimentation. If so, the conclusions can be very far off if interactions exist between the factors being plotted or examined numerically. The only way to take interaction into account is to run the experiments as factorial experiments and then derive the relations between the statistically significant factors and interactions using regression analysis. The effect of many kinds of variables can be determined by relatively small perturbations superimposed upon the total simulated field conditions, as by using the method of additions to study the effect of the concentration of Ca^{++} or other ions. Other factors, like temperature, surface area, soil type, etc., can be readily included. A number of factors can be included simultaneously with factorial experiments. (Models might be of help to point out possible-important factors that should be included in the experiments, but mental imagery, not mathematical formulations, ultimately provides the input for deciding what variables to include in experiments.) If the number of potential factors is large, it may be desirable to run screening experiments like main-effect factorial experiments first, possible followed by fractional factorials.

Even with the best kind of designs, the magnitude of the effect of only those factors purposely varied can be learned from the experiment, but some other factors may have an effect and even interact with the experimental factors. But if any unidentified factors can be kept at the same levels as they occur in the field (such as by using the same soil throughout the experiment because some unknown soil properties may be significant factors), then the effect of the known factors will be correctly estimated even if interaction does exist between them and the unidentified factors.

The graded serial batch extraction procedure provides the flexibility reliability, speed, and ease of interpretation needed to provide data for the derivation of empirical equations which contain a minimum of pitfalls for predicting the movement of hazardous substances through soil.

ACKNOWLEDGEMENTS

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DISPOSAL AND REMOVAL OF HALOGENATED HYDROCARBONS IN SOILS

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ABSTRACT

In this report, the adsorption, mobility, and degradation of polybrominated biphenyls (PBBs) and hexachlorobenzene (HCB) in soil materials and in a carbonaceous adsorbent were studied, together with the solubilities of PBBs and HCB in waters and landfill leachates. The aqueous solubilities of both materials were low ($<$ 16 ppb), but solubilities were higher in river water and landfill leachate than in distilled water. The solubilities can be directly correlated with the level of dissolved organics in the waters. By using a soil thin-layer chromatography technique, it was found the PBBs and HCB were immobile in all soils when leached with deionized water and landfill leachate; they were highly mobile in all soil materials when leached with organic solvents.

Freundlich adsorption isotherm plots of PBBs and HCB sorption on soils and on a carbonaceous adsorbent yielded straight and nearly parallel lines. All regression lines generated had a coefficient (r^2) of at least 0.98, which indicated an excellent fit of the data to the Freundlich equation. PBBs and HCB were found to be strongly adsorbed by the carbonaceous adsorbent and by soil materials, with HCB being adsorbed to a greater extent than PBBs. The adsorption capacity and mobility of PBBs and HCB were highly correlated with the organic carbon content of the soil materials.

In a soil incubation study, it was found that PBBs and HCB persisted for 6 months in soil with no significant microbial degradation. Because of their low water solubilities, strong adsorption, and persistence in soils, these two compounds are highly resistant to aqueous phase mobility through earth materials; however, they are highly mobile in organic solvents.

INTRODUCTION

Polybrominated biphenyls (PBBs) and hexachlorobenzene (HCB) are halogenated hydrocarbons. They belong to a class of aromatic halogenated organic compounds; these compounds are chemically similar to the more commonly known contaminant polychlorinated biphenyls (PCBs) and polychlorinated napthalene (PCN).

In 1973 PBBs were accidently added to livestock feed in place of magnesium oxide.[9, 28, 40] This incident has been called the most costly and disastrous contamination ever to occur in United States agriculture.[28] The contamination had a catastrophic impact on the Michigan livestock industry and resulted in thousands of farm animals being killed and buried. Altogether approximately 29,800 cattle, 5,920 swine, 1,470 sheep, and 1.5 million chickens were killed and buried by the end of 1975.[9]

The commercial production of PBBs began in 1970. Approximately 13.3 million pounds of PBBs were produced in the United States from 1970 to 1976.[38] About 11.8 million pounds of this total was hexabromobiphenyl (fireMaster BP-6, FF-1); the remaining 1.5 million pounds consisted of octabromobiphenyl and decabromobiphenyl. At the present time, no PBBs are being imported in commercial quantities. On the other hand, the export of PBBs from the United States to Europe has increased during the past several years and totaled 805,000 pounds in 1976.[38] The major uses of PBBs were for the production of flame retardant resins of acrylonitrite, bertadiene, and styrene for business machines, electrical housings, textiles, and other materials.[43, 14] All of these uses were discontinued in late 1974 as result of the Michigan incident.[14]

HCB is both a starting material and a by-product of the chemical industry.[16] Quinlivan, Ghassemi, and Santy[39] estimated that 3,909 metric tons of HCB are generated annually in the United States. Approximately

240 metric tons are used in industry; the rest is disposed of by incineration, or as wastes on the land. There are two major uses of HCB in industry: as a peptizing agent in the manufacture of styrene and nitroso rubbers for tires, and as a fungicide for agricultural seed treatment.[39] HCB is present in industrial waste as a by-product in several manufacturing processes, mainly in the commercial production of various chlorinated solvents such as carbon tetrachloride, perchloroethylene, dichloroethylene, and trichloroethylene. HCB has also been present as an impurity or by-product in the production of several pesticides such as dacthal, mirex, simazine, atrazine, propazine, and pentachloronitrobenzene.[39]

Mismanagement of HCB-containing wastes has resulted in several episodes of environmental contamination in the United States and abroad. The best documented case of an HCB episode occurred in southern Louisiana.[6, 7]

Many researchers have reported the effects of PBBs and HCB on organisms such as fish, birds, and mammals including humans.[24, 41, 35, 37, 42, 23, 26, 27, 45, 12, 36, 25, 31, 46] Both PBBs and HCB have a high bioaccumulation factor in fish.[24, 32] The major problem with regard to PBBs and HCB intake by man is that he resides at the top of most food chains. Therefore man can take in substantial amounts of PBBs and HCB even though only trace levels are present in meat, or in the water of streams and lakes. PBBs and HCB have been identified as a significant hazard to human health as well as to the environment;[27, 8] therefore, their disposal has caused great concern. Little information is presently available, however, concerning the mechanisms of attenuation of PBBs and HCB in earth materials, or concerning the possibility of groundwater contamination by PBBs and HCB being leached from landfills.

The limited amount of information presently available indicates that PBBs and HCB have a fairly strong affinity for soil. The mechanisms of transport of PBBs and HCB in the biosphere, and the mechanisms of attenuation in earth materials are unknown. Data on the factors affecting PBBs and HCB attenuation by soil materials, solubility in waters and landfill leachates, and mobility in soils would provide a useful basis for determining waste treatment methods, for predicting PBBs and HCB migration under landfills, and for selecting and designing future disposal sites.

The purposes of this project are: (*a*) to conduct a literature review of information on the attenuation of PBBs and HCB in soil materials; (*b*) to measure the solubility of PBBs and HCB in waters and landfill leachates; (*c*) to measure the adsorption capacity of selected soils and a carbonaceous adsorbent for PBBs and HCB; (*d*) to quantitatively evaluate the effects of adsorbent composition and of organic solvents on adsorption, and mobility of PBBs and HCB; (*e*) to use this data to develop a mathematical model that will assist in the prediction of PBB and HCB adsorption.

This research is supported in part by Grant R-804684-01-0, from the U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory, Solid and Hazardous Waste Research Division, Cincinnati, OH 45268. This is a report of work conducted as part of that grant, and the results should be considered preliminary and subject to reinterpretation if future results require it. Mention of trade names does not constitue endorsement.

METHODS AND MATERIALS

PBB and HCB Materials

FireMaster BP-6 (lot #6244A) was obtained from Michigan Chemical Corporation and was used without further purification. The product contained more than 30 isomers of polybrominated biphenyl (PBB) as identified in our laboratory using a SE-30 WCOT glass capillary gas chromatographic column and an electron capture detector (ECD). Several major isomers were identified: 2, 2', 4, 5, 5'-penta-; 2, 3', 4, 4', 5-penta-; 2, 2', 4, 4', 5, 5'-hexa-; 2, 2', 3, 4, 4', 5'-hexa-; 2, 3', 4, 4', 5, 5'-hexa-; 2, 2', 3, 4, 4', 5, 5'-hepta-; and 2, 2', 3, 3', 4, 4', 5, 5'-octabrominated biphenyl.[43, 29, 13]

Uniform ^{14}C-labeled-PBB (lot #872-244) was used in some studies and was synthesized and purified according to our specifications by New England Nuclear Corporation, Boston, Massachussetts. This product contained the two major isomers of fireMaster BP-6, approximately 65 percent 2, 2', 4, 4', 5, 5'-hexabromobiphenyl, and 35 percent 2, 2', 3, 4, 4', 5, 5'-heptabromobiphenyl. The specific activity of the ^{14}C-PBB was 9.34 mCi/mmole.

Hexachlorobenzene (HCB) was purchased from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. This product was recrystalized from distilled-in-glass hexane, and this process was repeated several times until the purity reached nearly 100 percent.

Uniform ^{14}C-labeled-HCB (lot #852-058) was purchased from New England Nuclear Corporation, Boston, MA. The specific activity was 35.5 mCi/mmole (.125 mCi/mg).

Adsorbents

Six earth materials and a carbonaceous adsorbent representing a wide range in characteristics were selected as adsorbents. The materials being studied are: Houghton muck, Catlin sil, Flanagan sicl, Ava sicl, Bloomfield ls, Ottawa silica sand, and Ambersorb^{R} XE-348. The carbonaceous adsorbent was selected because of its excellent performance characteristics in the removal of organic compounds at low concentrations.

Waters and Leachates

Distilled water, deionized water, Sugar Creek water, Blackwell landfill leachate, and DuPage landfill leachate were selected for use in the solubility study. Leachates were centrifuged through a continuous flow centrifugation apparatus (model JCF-Z, Beckman Instruments) at approximately 17,000 rpm, prior to passing through a 0.22 μm pore size Millipore^{R} cellulose acetate membrane. The Sugar Creek water was also passed through the 0.22 μm membrane before use.

Analytical Development

In general, PBBs are determined quantitatively by comparing gas chromatographic (GC) response patterns of a multicomponent environmental sample with the GC-response patterns of commercial PBBs. In practice, quantitative results are usually achieved by comparing the integration of the GC peaks obtained from the unknown mixture with the integration of the GC peaks obtained from a standard PBB mixture.

A PBB mixture contains a large number of isomers, and it was not possible to obtain a standard containing all isomers observed in this work. Therefore, the response of each PBB isomer relative to the response of an internal standard (hexabromobenzene) was used for quantification.

To accomplish this, an assumption was made that the response of the flame ionization detector (FID) was the same for all of the isomers of fireMaster BP-6. Such an assumption is plausible because each isomer has an equal number of carbon atoms. Thus, the percentage of each PBB isomer relative to the internal standard in a mixture of PBBs of known concentration was determined by GC using an FID. From these percentages and the same internal standard the response factors for individual PBB isomers were calculated for the electron capture detector (ECD). The ECD was used because it is specific to halogenated compounds and gives much lower detection limits for these compounds than can be achieved using FID. The results of the analysis showed that, in all cases, the overall standard deviation of error for PBB analysis ranged from 2.75 to 3.76 percent.

For the quantitative analysis of HCB, the same technique was used, except tribromobenzene was used as an internal standard. The standard deviation of error for 0.03 ppm and 0.05 ppm standards was less than 1 percent.

The samples and standards were analyzed on a Perkin-Elmer Sigma I gas chromatograph (GC) equipped with electron capture detection and flame ionization detection capabilities. The conditions for the gas chromatographic analysis for PBBs and HCB are shown in Table 1.

Solubility Studies

In the study of solubilities of PBBs and HCB in waters and leachates, 0.5 gm and 0.1 gm of fireMaster BP-6 or HCB were placed in 1-liter Erlenmeyer flasks. The flasks were then filled with distilled water, deionized water, Sugar Creek water, DuPage leachate, or Blackwell leachate. The mixture in each flask was agitated vigorously with a magnetic stirring bar coated with teflon. Water samples were collected after 2, 4, and 7 days for PBBs and 2, 7, and 30 days for HCB.

Solubility measurements were conducted by filtering 250-mL aliquots of PBB- or HCB-water solution through PBB- or HCB-saturated Millipore membranes (0.22 μm).

TABLE 1. CONDITIONS FOR GAS CHROMATOGRAPHIC ANALYSIS

Conditions	PBBs	HCB
Column	6 ft x 2 mm I.D. glass column (or stainless column for FID). 3 percent SE-30 on 80/100 mesh chromosorb WHP	6 ft x 2 mm I.D. glass column, 5 percent OV-17 on 80/100 mesh chromosorb WHP
Injector temperature	270°C	250°C
Column temperature	250°C	200°C
Detector temperature	300°C	300°C
Carrier gas	Methane/argon (helium for FID), flow 40 mL/min	Methane/argon, flow 35 mL/min

A separate study had shown that the adsorption capacity for PBB or HCB of the cellulose acetate membrane used to filter the PBB or HCB solution could be saturated by soaking the membrane in a fresh 300-mL aliquot of PBB- or HCB-saturated water each day for 3 days, followed by flushing with 200 mL of PBB or HCB saturated water.

Two 100-mL aliquots of the filtrates were then extracted with 10, 5, and 5 mL of water-saturated hexane. Hexabromobenzene or tribromobenzene (0.25 μg) was added as an internal standard to the PBB or HCB extracts, respectively. The extracts were then concentrated to 1.0 mL and analyzed by GC. A representative chromatogram is shown in Figure 1.

The solubilities of major PBB isomers and HCB in waters and leachates are shown in Tables 2 and 3 respectively. The results show that the solubility of PBBs and HCB was very low. The average solubilities of PBBs in distilled water, deionized water, Sugar Creek water, DuPage leachate, and Blackwell leachate were 0.057 μg/L, 0.317μg/L, 0.497 μg/L, 8.889 μg/L, and 16.892 μg/L, respectively, and the solubilities of HCB in the same waters and leachates were 1.75 μg/L, 1.78 μg/L, 2.22 μg/L, 4.14 μg/L, and 4.47 μg/L, respectively. The higher solubilities of both compounds in the river water and leachates were correlated with the level of dissolved organic material in the waters.

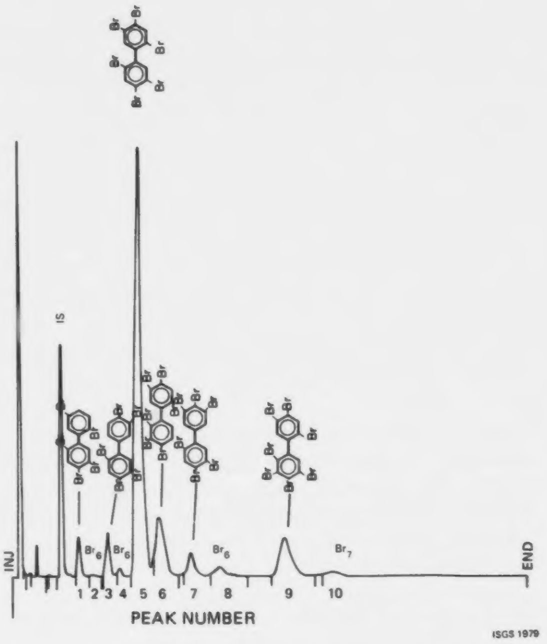

Figure 1. Gas chromatogram of the PBB mixture fireMaster BP-6 on 6-ft glass column packed with 3% SE-30 on 80/100 mesh Chromosorb WHP.

TABLE 2. SOLUBILITY OF THE MAJOR PBB ISOMERS IN WATERS AND LEACHATES (μg/L)*

	Distilled water			Deionized water			Sugar Creek water			Du Page leachate			Blackwell leachate		
Peaks	2 days	4 days	7 days	2 days	4 days	7 days	2 days	4 days	7 days	2 days	4 days	7 days	2 days	4 days	7 days
1	. . .	. . .	. . .	0.030	0.029	0.035	0.038	0.034	0.043**	0.461	0.501	0.448**	0.610	0.660	0.721**
2	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	0.242	0.240	0.244	0.490	0.498	0.520
3	. . .	. . .	. . .	0.040	0.038	0.045	0.040	0.039	0.044	0.901	1.005	0.760	1.415	1.373	1.467
4	0.001	0.002	0.001	. . .	. . .	. . .	0.005	0.004	0.006	0.178	0.210	0.163	0.306	0.314	0.333
5	0.035	0.032	0.038	0.136	0.142	0.125	0.165	0.161	0.190	2.605	2.686	2.417	5.615	5.097	6.141
6	0.004	0.003	0.004	0.059	0.050	0.064	0.067	0.087	0.089	1.673	1.979	1.457	3.000	2.979	3.149
7	. . .	. . .	. . .	0.017	0.016	0.015	0.039	0.037	0.042	0.910	0.923	0.788	1.857	1.709	1.901
8	. . .	. . .	. . .	0.009	0.008	0.015	0.037	0.039	0.038	0.510	0.490	0.469	0.773	0.756	0.711
9	0.017	0.019	0.016	0.028	0.025	0.026	0.080	0.074	0.084	1.050	1.203	0.930	1.925	1.908	2.136
10	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	0.430	0.427	0.368	0.790	0.725	0.798
Total	0.057	0.056	0.059	0.319	0.308	0.325	0.481	0.475	0.536	8.960	9.664	8.044	16.781	16.019	17.877

*Each value is a mean of 2 replications.

**Each value is mean of 4 replications (two separate sets).

TABLE 3. SOLUBILITY OF HCB IN WATERS AND LEACHATES

Waters and leachates	Concentration (μg/L)*		
	2 days	7 days	30 days
Distilled water	1.77	1.71	1.75
Deionized water	1.83	1.67	1.78
Sugar Creek water	2.43	2.35	2.22
Du Page leachate	4.17	4.04	4.14
Blackwell leachate	4.58	4.29	4.47

*Each value is the mean of 2 replicates.

A similar finding on PBBs had also been reported elsewhere.[30] These results indicate that PBBs were greater than 200 times and HCB greater than 2.5 times more soluble in landfill leachates than in "pure" waters. The type of dissolved organic matter is also important in determining how soluble the compound will be in a given water. These factors should be taken into account when attempting to predict the migration of these compounds from waste disposal sites.

Adsorption Studies

Equilibrium adsorption studies were carried out by shaking known volumes of PBB and HCB solutions with varying weights of soil materials and carbonaceous adsorbent at a constant temperature of 22°C. The rate of adsorption of PBBs and HCB by soil materials and carbonaceous adsorbent was rapid. Equilibrium conditions were achieved in less than 4 hours. The adsorption data were fitted by linear regression to the log form of the empirical Freundlich adsorption equation:

$$\log \frac{x}{m} = \log K + 1/n \log Ceq$$

where x = μg of compound adsorbed, m = weight of adsorbent (g), Ceq = equilibrium concentration of the solution (μg/mL or ng/mL), and K and 1/n are constants.

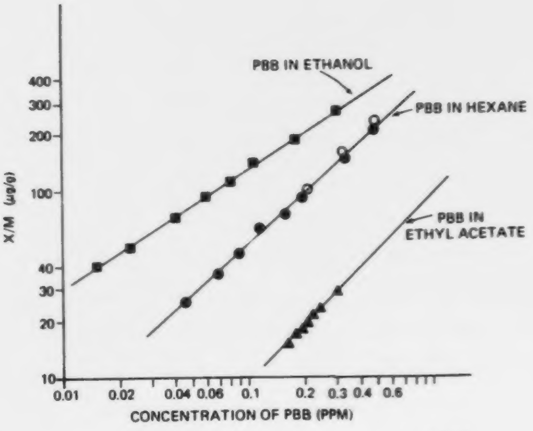

Figure 2. Freundlich adsorption isotherms of PBB and ^{14}C-PBB adsorption on Ambersorb XE-348 from organic solvents at 22°C ± 1°C. Open symbols indicate analysis by GC.

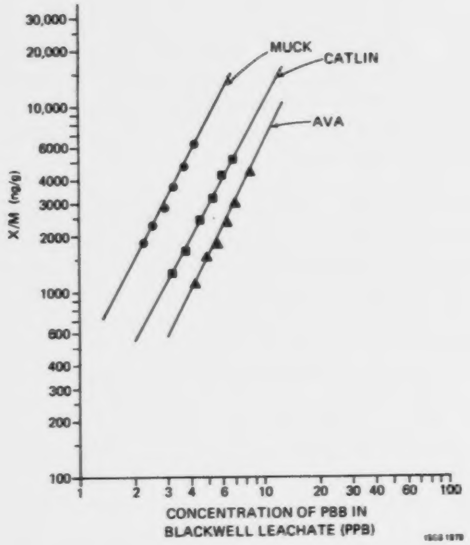

Figure 3. Freundlich adsorption isotherms of PBBs on three soil materials from Blackwell leachate at 22°C.

The use of this relation allows quantitative predictions of PBBs and HCB adsorption–by a given adsorbent–over the concentration range of water-, leachate-, and organic solvent-soluble PBBs and HCB.

Freundlich adsorption isotherm plots of PBBs and HCB sorption on Ambersorb XE-348 and on each soil type yielded straight and nearly parallel lines. The adsorption isotherms for PBBs are shown in Figures 2 and 3. Similar isotherms were obtained for HCB sorption. Values of K and 1/n were obtained from the calculated linear regression equations as the intercept and slope, respectively, of the adsorption data. The calculated Freundlich constants are shown in Tables 4 and 5. All regression lines generated had a coefficient (r^2) of at least 0.98, which indicates an excellent fit of the data to the Freundlich equation.

PBBs and HCB were found to be strongly adsorbed

TABLE 4. FREUNDLICH K (μg/g), 1/n, AND REGRESSION COEFFICIENT, r^2 FOR THE ADSORPTION OF ^{14}C-PBB AND ^{14}C-HCB FROM VARIOUS ORGANIC SOLVENTS BY AMBERSORB XE-348

	Freundlich parameters					
	K		1/n		r^2	
Solvents	PBB	HCB	PBB	HCB	PBB	HCB
Ethanol	578	2690	0.64	0.71	0.9982	0.9945
Hexane	389	625	0.88	0.69	0.9995	0.9989
Ethyl acetate	98	804	1.03	0.80	0.9929	0.9977
Ethyl dichloride	ND	228	ND	0.70	ND	0.9924

ND = Not determined.

by Ambersorb XE-348 and by soil materials. In all studies, HCB had a greater adsorption tendency than PBBs. The adsorption of PBBs and HCB for the three soils followed the series, muck > Catlin > Ava.

The PBB adsorption constant (K) plotted as a function of TOC gave a very high correlation. Similar results for PCBs were also reported elsewhere.[33] The calculated linear regression relation was:

$$K = 64.92 + 17.57\ \text{TOC}$$

$$r^2 = 0.999$$

A similar result was also found for HCB on the same adsorbates. The HCB adsorption constant (K) in log form plotted as a function of TOC also showed a very high correlation. The calculated linear regression relation was:

$$\log K = 2.01 + 0.10\ \text{TOC}$$

$$r^2 = 0.999$$

The adsorption of hexane- and ethanol-soluble ^{14}C-PBB and ^{14}C-HCB by Catlin and muck soils was also investigated. The results showed that virtually no adsorption took place. This result strongly indicates that potential migration of PBBs and HCB in a landfill could occur if the PBB and HCB wastes were dissolved in organic solvents or if organic solvents were disposed of in the same landfill location.

TABLE 5. FREUNDLICH K (μg/g), 1/n, AND REGRESSION COEFFICIENT (r^2) FOR THE ADSORPTION OF PBB AND ^{14}C-HCB BY VARIOUS SOILS FROM AQUEOUS SOLUTION

	Freundlich parameters					
	K		1/n		r^2	
Soils	PBB	HCB	PBB	HCB	PBB	HCB
Houghton Muck	361	4193	1.99	1.12	0.9918	0.9985
Catlin sil	144	276	1.89	0.99	0.9820	0.9906
Ava sicl	88	136	1.77	0.93	0.9790	0.9880

Mobility Studies: Determination by Soil TLC

The technique of determining pesticide mobility in soils by soil TLC was introduced by Helling and Turner.[20] Since the introduction of the technique, the mobility of a large number of pesticides in a variety of soils have been tested.[21, 22, 23] Soil TLC is a laboratory method that uses soil as the adsorbent phase and a developing solvent (water, leachate, organic solvent, etc.) in a TLC system.

The methods used to prepare soil TLC plates has been reported previously by Griffin.[19] In these studies, the ^{14}C-PBBs, ^{14}C-HCB, and non-^{14}C-labeled-PBBs and HCB were spotted 2 cm from the base and leached 12 cm with an acetone, acetone/water mixture (1:1, v/v) and DuPage leachate; they were also leached 10.5 cm with water, methanol, and dioxane. For the fireMaster BP-6 mixture, the plates were leached 10.5 cm with acetone/water (1:1, and 8:2, v/v), acetone, and carbon tetrachloride. The plates were immersed in 0.5 cm of the various solvents in a closed glass chamber and were removed when the wetting front reached the 12 cm or 10.5 cm (distance) line. The soil plates were removed and air dried. Soil increments of 1 cm, starting 1.5 cm above the base of the plate, were scraped off. The soils were placed in a glass centrifuge and/or test tubes and extracted with suitable organic solvents. The concentration of ^{14}C-labeled compounds was determined with standard liquid scintillation techniques. With non-^{14}C-labeled compounds, the concentration in the extracts was measured by GC analyses.

The R_f values are shown in Table 6. The results show that under the conditions tested, PBBs and HCB were immobile in these earth materials when leached with water and DuPage leachate, but were highly mobile when leached with organic solvents. The mobility of PBBs and HCB in earth materials was directly proportional to the solubility of the compounds in the leaching solvents and indirectly proportional to the soil organic matter content. The mobility of PBBs and HCB in the tested earth materials was: Ottawa sand > Bloomfield sand > Ava soil > Flanagan soil > Catlin soil. A similar finding for PCBs was reported elsewhere.[18] It was also observed that PBBs were extremely mobile in Catlin soil when leached with carbon tetrachloride.

TABLE 6. MOBILITY OF PBBs AND HCB IN SEVERAL SOIL MATERIALS LEACHED WITH VARIOUS SOLVENTS AS MEASURED BY SOIL TLC

Soil materials	R_f values*											
	Water		Du Page leachate		Acetone/water (1:1, v/v)		Methanol		Acetone		Dioxane	
	PBB	HCB	PBB	HCB	PBB	HCB	PBB	HCB	PBB	HCB	PBB	HCB
Catlin sil	0.00	0.00	0.00	0.00	0.01	0.00	0.40	0.40	0.69	0.45	1.00	0.99
Flanagan sicl	ND	...	0.00	0.00	...	...	0.60	0.44	...	...	1.00	1.00
Ava sicl	0.00	0.00	0.00	0.00	0.02	0.01	0.61	0.48	0.76	0.80	1.00	1.00
Bloomfield ls	...	...	0.00	0.00	...	...	0.86	0.72	...	...	1.00	1.00
Ottawa s	0.00	0.00	0.00	0.00	0.17	0.02	1.00	0.99	0.99	1.00	1.00	1.00

*Computed from statistical peak analysis of data by using values of first moment for grouped data.
ND = Not determined.

PBBs and HCB are non-polar by nature and have very low solubility in water. Measurements of solubility of PBBs have yielded values of 0.497 and 16.892 ppb in river water and leachate, and the solubility for HCB to be 2.22 and 4.47 ppb in river water and leachate; however, PBBs and HCB are very soluble in organic solvents such as dioxane, carbon tetrachloride, acetone, methanol, etc. It is interesting that the mobilities of PBBs and HCB in earth materials were dramatically reduced when leached with an acetone/water mixture (Table 6). Separate studies have shown that the mobility of the major PBB isomers increased when the percentage of water decreased in the acetone/water mixtures. Another study also demonstrated that no PBB or HCB was retained in soil columns when ethanol, containing ^{14}C-PBB or ^{14}C-HCB, was percolated through the columns. This data again confirmed our previous findings on soil TLC plates. It showed that nearly 100 percent of ^{14}C-PBBs and ^{14}C-HCB were recovered from soil columns when percolated with organic solvent. This data agreed with our adsorption studies, which showed no significant amount of organic-soluble PBBs or HCB were adsorbed by soils.

This finding is significant in the disposal of PBBs and HCB wastes. To prevent potential migration of PBBs and HCB in a landfill, PBB and HCB wastes and organic solvents should not be disposed of in the same landfill location, and neither compound should be allowed to come in contact with leaching organic solvents.

Degradation Studies

The susceptibility of PBBs and HCB to biodegradation was evaluated using Catlin silt loam soil. Thirty grams of air-dried soil, which had passed through a 2 mm sieve, was placed in 250-mL Erlenmeyer flasks. One-third of the set of flasks were sterilized with propylene oxide. Sterilization was confirmed by inoculating a loopful of soil on a nutrient broth agar slant and finding no microbial growth after one week of incubation. Half of the non-sterilized flasks were inoculated with 5 mL of mixed culture,[11] which had previously been found to degrade water-soluble PCBs.

In the soil incubation studies, known amounts of PBBs or HCB were distributed dropwise on the soil. All soil samples were moistened with sterilized deionized water to approximately 35 percent of field capacity, then sealed with a sterilized rubber stopper wrapped in aluminum foil. Samples were then incubated in the dark at 22°C ± 2°C for 0, ½, 1, 2, and 6 months.

Three replicates of each treatment were extracted with a suitable organic solvent after the indicated period. The PBB or HCB extracts were each concentrated to 100 mL, and 1 mL of this extract was then diluted to 3 mL by adding 0.75 μg of hexabromobenzene or tribromobenzene in solvent as internal standards. The diluted extracts were then analyzed by GC.

The recovery of PBB components and HCB after incubation in sterilized and non-sterilized Catlin soil are shown in Tables 7 and 8. The data clearly show that PBB and HCB persisted for 6 months in soil with no significant microbial degradation. The same pattern of persistence holds for PBB incubation with mixed cultures added, which had previously shown effective degradation of water-soluble PCBs.[11] This data agreed with previous findings.[29,30] The persistence of PBBs and HCB is also consistent with evidence reported for PCBs which shows that the more heavily chlorinated isomers (penta or greater) are resistant to degradation,

TABLE 7. RECOVERY OF PBB ISOMERS AFTER INCUBATION OF 10 ppmw IN CATLIN SOIL,* IN PERCENTAGES

Incubation time (months)	Peak 1			Peak 3			Peak 4			Peak 5		
	S[†]	N-S[‡]	I[#]	S	N-S	I	S	N-S	I	S	N-S	I
0	82.1	83.2	83.7	84.5	85.3	84.6	89.5	91.3	90.5	91.2	93.8	92.5
½	80.9	80.4	81.5	81.3	85.5	87.5	80.3	87.7	88.1	84.9	88.9	86.9
1	79.5	80.0	81.7	79.8	81.3	81.5	81.0	84.8	86.8	83.3	87.8	85.4
2	73.4	74.5	76.1	74.3	75.0	75.9	80.4	86.1	88.3	81.9	84.5	84.0
6	73.1	75.3	74.2	73.2	75.4	75.6	79.3	86.8	85.7	80.5	83.0	83.3
	Peak 6			Peak 7			Peak 8			Peak 9		
0	89.9	92.9	90.4	91.7	93.1	94.2	90.8	91.6	92.5	91.9	94.1	93.3
½	85.1	89.8	86.1	86.9	88.4	89.5	85.3	87.9	88.3	87.7	89.1	88.4
1	84.0	88.7	84.5	84.7	84.0	87.7	84.1	86.6	87.1	87.8	89.7	91.9
2	82.5	84.3	82.3	82.9	83.6	85.9	82.0	86.4	86.2	85.6	86.8	87.4
6	81.9	83.1	82.8	80.9	84.0	84.3	83.0	87.2	86.4	84.7	84.7	85.1

*Each value is the mean of three replications

[†] S = Sterilized soil

[‡] N-S = Non-sterilized soil

[#] I = Inoculated mixed culture

though many lesser chlorinated components are metabolized.[1, 5, 44, 11] Of interest is the significant loss of extractability with time of all PBB isomers (Table 7) and HCB (Table 8) in the sterile as well as the nonsterile treatments. The loss of extractability of PBBs and HCB from soil is probably due to sorption, masking, or volatilization during long-term incubations.

We examined the fate of photodegraded PBB because the higher brominated forms are readily degraded by ultraviolet light to lesser brominated forms that could be more toxic. It can be reasoned that the PBB on PBB-amended soil surfaces might be subjected to some photodegradation; however, this does not appear to have been a significant reaction in the long-term incubation studies since the ratios of peaks 1:5:9 found in most of the PBB-amended soil extracts were (5.3:100:18.5), which did not vary significantly from the PBB standard (5.3:100:18.6).

TABLE 8. PERCENT OF HCB RECOVERED AFTER INCUBATION OF 3.33 ppmw IN CATLIN SOIL

Treatment	% of HCB remaining in soil			
	0 month	1 month	2 months	6 months
Sterilized	85.68*	82.78	79.75	63.26
Non-sterilized	89.04	84.08	82.24	64.74

*Each value is a mean of 3 replicates.

For a liquid culture study, a culture of mixed bacteria was used that was isolated from a Hudson River sediment from the Fort Miller disposal site in New York.[34] The predominant organisms found in the mixed culture were *Alkaligenes odorans*, *Alkaligenes denitrificans*, and an unidentified bacterium.[11] The culture was tested to determine if these organisms could metabolize any of the PBB isomers or HCB when present in a mineral growth medium:[17]

KNO_3	1.0 g/L	$FeCl_3$	0.02 g/L
$MgSO_4$	0.2 g/L	NaCl	0.1 g/L
$CaCl_2$	0.1 g/L	K_2HPO_4	1.0 g/L

The deionized water used to make up this medium was saturated with PBBs and/or HCB.

For these studies, 10 mL of a 3-day-old culture were added to 200 mL of mineral medium with PBB and/or HCB-saturated water. The solutions were shaken at 23° ± 2°C on a rotary shaker for 0, 2, and 4 weeks. Part of the samples were used as a control without adding inoculum. After an indicated period of time, two samples of each treatment were extracted with water-saturated hexane, then concentrated to 1 mL prior to GC analysis.

The results showed that no PBB or HCB metabolites were found in PBB- and HCB-saturated mineral solutions after 4 weeks. Apparently these mixed cultures cannot degrade fireMaster BP-6 or HCB.

Because PBBs are not degraded, are not leached in aqueous solutions, are not taken up by plants,[10] and are not volatilized (because of their low vapor pressure), we expect PBB to be a rather permanent component of contaminated soils. The same conclusion is probably true for HCB if the wastes are well-covered with compacted wet soil to prevent volatilization losses[15] in landfill sites.

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MOVEMENT AND BIOLOGICAL DEGRADATION OF LARGE CONCENTRATIONS OF SELECTED PESTICIDES IN SOILS

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ABSTRACT

Equilibrium adsorption isotherms of the non-linear Freundlich type were obtained for atrazine, methyl parathion, terbacil, trifluralin, and 2,4-D and four soils. Pesticide solution concentrations used in the study ranged from zero to the aqueous solubility limit of each pesticide. The mobility of each pesticide increased as the concentration of the pesticide in the soil solution phase increased. These results were in agreement with the equilibrium adsorption isotherm data. Biological degradation of each pesticide was measured by $^{14}CO_2$ evolution resulting from the oxidation of uniformly ^{14}C ring-labeled pesticides, except trifluralin which was labeled at $^{14}CF_3$. Technical grade and formulated forms of each pesticide at concentrations ranging from zero to 20,000 μg/g of soil were used in the biological degradation experiments. Pesticide degradation rates and soil microbial populations generally declined as the pesticide concentration in the soil increased; however, some soils were able to degrade a pesticide at all concentrations studied, some soils degraded a pesticide at a low concentration but not a higher concentration, while others remained essentially sterile throughout the incubation period. Total CO_2 evolution was not always a good indication of pesticide degradation. Several pesticide metabolites were formed and identified in various soil-pesticide systems. The quantities of methyl parathion, trifluralin and atrazine "bound" to the soil at the end ot the incubation period were measured and in some cases appeared to be related to types of metabolites formed during biological degradation.

INTRODUCTION

Because of a continued increase in the number and quantity of pesticide compounds being placed on the market, the safe disposal of surplus and/or waste pesticide materials has become an acute problem (von Rumker, et al., 1974). Incineration, encapsulation, isolation in underground caves and mines, chemical stabilization, land spreading and landfills are some of the procedures being considered for the disposal of pesticides and other hazardous wastes (Schomaker, 1976; von Everdingen and Freeze, 1971; Wilkinson, et al., 1978). Of these methods, disposal by landfills and land spreading appear to be more common and economical (Fields and Lindsey, 1975; Lindsey, et al., 1976). Placing hazardous wastes in the land has come under attack recently (Atkins, 1972; Rouston and Wildung, 1969) because there is no guarantee that the hazardous chemicals disposed of in this manner will not migrate from the disposal site to potable water supplies.

In general, pesticide applications associated with agricultural production have had very little adverse effect on the soil microbial activity (Cole, 1976; Hubbell, et al., 1973; Kaiser, et al., 1970, Newman and Downing, 1958; Roslycky, 1977). However, reports on soil microbial activity where large concentrations were used have been contradictory and inconclusive. For example, Ou et al. (1978a) observed 2,4-D (2,4-dichlorophenoxyacetic acid) degradation at concentrations of 5,000 and 20,000 μg/g of soil (ppm) for one soil type and no degradation at the same concentrations for another soil. Soil respiration and bacterial, fungal and actinomycete populations were significantly reduced in the soil unable to degrade 2,4-D. They concluded that the physical and chemical properties of the soil as well as the 2,4-D concentration were important factors in governing microbial activity and pesticide degradation in soils receiving large pesticide concentrations.

Trifluralin (α,α,α-trifluro-2,6-dinitro-N, N-dipropyl-p-toluidine) and atrazine (2-chloro-4-ethylamine-6-isopropylamino-s-triazine) are commonly used herbicides. Trifluralin applications of 3 kg/ha (1.4 ppm) have been shown not to influence soil bacterial, fungal and actinomycete populations significantly (Tyunaeva, 1974). However, when 1.1 kg/ha (0.5 ppm) was applied per year over a five year period, bacterial populations were inhibited while fungal and actinomycete populations were enhanced (Breazeale and Camper, 1970). When analytical grade trifluralin was incorporated into the soil at concentrations of 5,000 ppm, CO_2 evolution and bacterial populations were inhibited while streptomycete populations were stimulated. Stojanovic et al. (1972) has shown that formulated trifluralin stimulated CO_2 evolution and streptomycete populations while inhibiting bacterial populations in soil. Atrazine was shown not to inhibit soil respiration at concentrations associated with agricultural production (Kaiser, et al., 1970; Eno, 1962). Cole (1976) and Voets et al. (1974) have shown that soil bacterial and fungal populations were not affected at rates below 4 kg/ha (1.8 ppm). However, Stojanovic et al. (1972) reported that atrazine inhibited soil respiration and bacterial populations at 5,000 ppm but had no effect on fungal populations.

A thorough understanding of the various processes that influence the persistence, retention, and leaching of pesticides in soils is required to develop technology for the selection and management of pesticide disposal sites involving soils. The fate of pesticides in soils when applied at concentrations similar to those associated with agricultural practices has been well-documented in several reviews (Bailey and White, 1970; Sanborn, et al., 1977). However, the direct extrapolation of this data base to systems containing large pesticide concentrations, such as those occurring at or below disposal sites, may not be feasible (Davidson et al., 1976).

Laboratory experiments were initiated to investigate the physical, chemical and microbiological behavior of five pesticides in four soils when the pesticide was present at large concentrations. The objectives of the study were to: 1) Measure and describe pesticide adsorption in selected soil-water systems over a wide range of chemical concentrations (zero to water solubility), 2) Measure mobility and distribution of pesticides in selected soils, when applied or initially present in soil at large concentrations, 3) Measure chemical and microbial degradation rate, and identify metabolites produced in soil-pesticide systems receiving large pesticide concentrations, and 4) Measure the influence of large pesticide concentrations on soil microbial activity and respiration rate for selected soil-pesticide systems.

MATERIALS AND METHODS

Soils

Soils used in this study were: Webster silty clay loam (Mollisol) from Iowa, Cecil sandy loam (Ultisol) from Georgia, Glendale sandy clay loam (Entisol) from New Mexico, and Eustis fine sand (Entisol) from Florida. These soil types were selected on the basis of their geographic and taxonomic representation of major U. S. soils. Surface samples (0-30 cm) of each soil were air-dried and passed through a 2-mm sieve prior to storage and use. Selected physical and chemical properties of the mineral soils are given in Table 1.

Pesticides

Five pesticides included in this study were: 2,4-D (2,4-dichlorophenoxyacetic acid), atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine), terbacil (3-tert-butyl-5-chloro-6-methyluracil), methyl parathion (O-O-dimethyl O-p-nitrophenyl phosphorothioate), and trifluralin (α,α,α-trifluoro-2,6-dinitro-N, N-dipropyl-p-toluidine).

Adsorption Experiments

Equilibrium adsorption isotherms for all soil-pesticide combinations were measured using the batch procedure. Equilibrium was achieved by shaking duplicate samples of five or ten grams of soil with

TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF THE SOILS USED IN THIS STUDY

SOIL	PARTICLE SIZE FRACTION (%) sand	silt	clay	pH (1:1 paste) Water	1N KCl	CEC (meq/100 g)	Organic C (%)
Webster	18.4	45.3	38.3	7.3	6.5	54.7	3.87
Cecil	65.8	19.5	14.7	5.6	4.8	6.8	0.90
Glendale	50.7	16.4	22.9	7.4	6.5	35.8	0.50
Eustis	93.8	3.0	3.2	5.6	4.1	5.2	0.56

10 ml of pesticide solution in pyrex screw-cap glass test tubes for 48 hours. Preliminary experiments had indicated that no measurable increase in pesticide adsorption occurred after 48 hours. Following equilibrium, the test tubes were centrifuged at 800 x G for ten minutes and the ^{14}C-activity in one-ml aliquots of the clear supernatant solution was counted by the liquid scintillation method. Decreases in pesticide solution concentration were attributed to adsorption by the soil. All adsorption experiments were performed at a constant temperature (23±1 C).

Column Displacement Experiments

Pesticide movement through water-saturated columns of soil was studied (Rao and Davidson, 1979) using the miscible displacement technique described by Davidson et al. (1968). The air-dry soil was packed in small increments into glass cylinders (15 cm long, 45 cm^2 cross-sectional area). Medium porosity fritted glass end plates served to retain the soil in the column. The soil was initially saturated with 0.01 N $CaCl_2$ solution. A known volume of pesticide solution at a desired concentration was introduced to the soil at a constant flux using a constant-volume peristaltic pump. After a specific volume of pesticide solution had been applied, the pesticide solution was subsequently displaced through the soil column with 0.01 N $CaCl_2$ at the same soil-water flux. Effluent solutions were collected in 5 or 10 ml aliquots using an automatic fraction collector. A pulse of ^3H_2O (specific activity 5 nCi/ml) was also displaced through each soil column to characterize the transport of non-adsorbed solutes. The activity of ^{14}C and ^3H_2O in effluent fractions was counted by liquid scintillation. All displacements were performed at a Darcy flux of approximately 0.22 cm/hr to ensure near-equilibrium conditions for pesticide adsorption during flow. The total volume of water held in the soil column was gravimetrically determined at the end of each displacement by extruding the soil from the glass cylinder and oven drying. The number of pore volumes (V/V_0) of solution displaced through the soil column was calculated by dividing the cumulative outflow volume (V) by total water volume (V_0) in the soil column. Effluent pesticide concentrations were expressed as relative concentrations (C/C_0), where C and C_0 are, respectively, effluent and input concentration. Plots of C/C_0 versus V/V_0 are referred to as breakthrough curves (BTC).

For the leaching or infiltration experiments, air-dry soil was packed into 3.2-cm diameter lucite cylinders composed of 1-cm sections supported by a V-shaped container that permitted observation of the wetting front position with time. Technical or analytical grade pesticide was dissolved in benzene and was spiked with ^{14}C-labeled compound. The benzene solution was mixed with air-dry soil (to give 200 or 2,000 μg of pesticide/g of soil and 10 nCi/g soil) and the benzene evaporated. In order to simulate a waste disposal site, the pesticide-spiked soil was packed into the top 1.5 cm of the soil column. Infiltration of water into horizontal columns of soil was controlled by maintaining the soil surface at a negative pressure (-4 cm of water) using a fritted-glass plate and a constant-head burette. The fritted-glass plate apparatus was filled with 0.01 N $CaCl_2$ and the desired negative pressure applied before it was placed in contact with the soil. Measurement of time in all experiments commenced the instant contact was established between the fritted-glass plate and soil surface. Water entering the soil was measured volumetrically using a constant-head burette connected to the fritted-glass plate apparatus. Measurements of distance to the wetting front (zero at the contact plane between soil and plate) were visually observed. When flow had proceeded for the desired time (i.e., until the wetting front had advanced to about 30 cm), the water supply was discontinued and the soil column was immediately cut into 1-cm segments. About one-half of the soil contained in each 1-cm segment was oven-dried at 105° C for 24 hours to determine the gravimetric soil-water content. The remaining one-half of the soil from each 1-cm-segment was dried in a vacuum desiccator over P_2O_5 or H_2SO_4 for a 24-48 hour period. About 0.5-0.7 g of the desiccator-dried soil was then combusted in a Packard Model 306B sample oxidizer; the $^{14}CO_2$ evolved by combustion was trapped in a premixed organic amine-fluor cocktail and assayed by liquid scintillation. The pesticide concentrations were calculated using the specific activity (dpm/μg pesticide) of the pesticide-spiked soil sample. The pesticide concentrations determined in the above manner represent the sum of adsorbed and solution-phase concentrations and were expressed as μg pesticide/g oven-dry soil.

Pesticide Degradation

Each soil was initially wet to a soil-water content corresponding to 30% of the 0.33 bar soil-water tension and incubated for one week at 25 C. Following incubation, each soil was then mixed thoroughly with a specific quantity of pesticide and sufficient water was added to bring the soil up to 0.33 bar soil-water tension. For pesticide degradation and soil respiration experiments, 100 gms (oven-dry basis) of each pesticide-treated soil was placed in a 250 ml Erlenmeyer flask. Special care was then taken when mixing the pesticide with the soil to ensure a uniform distribution of the pesticide within the soil. Technical grade and formulated materials of each pesticide were used. The flasks were then connected to a plexiglass manifold and CO_2-free water-saturated air passed through the manifold into the flasks at a flow rate of 10 ml/min per flask. For pesticides with a high vapor pressure, the air leaving the flask was passed through 40 ml of ethylene glycol to absorb the volatilized pesticide. The air leaving each flask was also bubbled through a KOH solution (0.1 - 0.2N) to absorb the evolved CO_2. At frequent intervals, the KOH solutions were replaced with fresh KOH solutions and the CO_2 concentrations determined by titration. ^{14}C-CO_2 activity in the KOH solution was determined by liquid scintillation counting.

Metabolite Identification

Soil treatments and incubation were essentially the same as for the pesticide degradation experiments, except 150 g of soil were used and 2 μCi ^{14}C-pesticide per 100 g soil were added. Ten gram soil samples were withdrawn biweekly. The soil samples were extracted three times with the appropriate solvent (Table 2). The 20,000 μg/g samples were extracted four times because of their high pesticide concentrations. The extracted soil was then air dried and stored in a cold chamber prior to analysis for "bound" ^{14}C. The extracts were concentrated to 10 ml on a rotary evaporator, or in a Danish Kuderna evaporator, then further concentrated using a gentle stream of N_2 and an aliquot was assayed for ^{14}C. The extracts were further concentrated with N_2 to one ml and an aliquot equivalent to 15,000 dpm of each sample was streaked on a thin layer plate. The TLC plates were developed and placed on Kodak on-screen x-ray film (NS-57) for one month. Radioactive streaks on the TLC plates were scraped and the radioactivity eluted with two ml of solvent (Table 2). The percentage of radioactivity in each separate radioactive component on the TLC plates was determined by liquid scintillation counting.

The unextractable "bound" portion of the ^{14}C-residue was determined by oxidizing the extracted soil samples in a stream of O_2 at 800° C according to the modified method of Watts (1971). The air dried extracted soil was placed directly in the oven at 800° C and the O_2 stream which passed through the soil was bubbled directly into 15 ml of phenethylamine CO_2-trapping cocktail solution. Complete combustion took approximately five minutes. Then N_2 was purged through the system to eliminate O_2 and the trapped $^{14}CO_2$ was assayed.

TABLE 2. SOLVENTS USED FOR PESTICIDE EXTRACTION FROM SOIL

Pesticide	Solvent
2,4-D	Ether Ethyl
Trifluralin	1) Benzene/Ethyl Acetate (3:1)
	2) MeOH
Atrazine	MeOH (soxhlet)
Methyl Parathion	Hexane:Acetone (80:20)

RESULTS AND DISCUSSION

Adsorption Experiments

Equilibrium adsorption isotherms were determined for each soil-pesticide combination by measuring pesticide adsorption at five or more concentrations ranging from zero to the pesticide's aqueous solubility. All adsorption isotherms considered in this study, with the exception of 2,4-D and the Glendale soil, were described by the Freundlich equation ($S = KC^N$), where K and N are constants, and S and C are adsorbed (μM/kg soil) and solution (μM/l) phase pesticide concentrations. The values of the Freundlich adsorption constants, K and N, for each soil-pesticide combination studied were obtained using a least-square fit procedure to the adsorption data. These values are presented in Table 3.

Two important conclusions can be made based on the data presented in Table 3. First, the fact that the Freundlich equation describes nearly all pesticide adsorption isotherms over a wide concentration range suggests that adsorption sites were not saturated at any concentration considered in this study. The amount of pesticide adsorbed by the soil continued to increase, at a decreasing rate, with each increase in solution concentration. The behavior may not, however, hold for other pesticide adsorbents (Weber and Usinowicz, 1973). Second, contrary to a frequent assumption, pesticide adsorption isotherms are generally nonlinear, that is, N is greater or less than one (Table 3). Linear adsorption isotherms have been generally accepted for low pesticide concentrations because it simplified computer simulation modeling (Davidson et al., 1968; Davidson and Chang, 1972; Hugenberger et al., 1972; Kay and Elrick, 1967).

Because soil organic carbon content generally correlates well with pesticide adsorption, the use of an adsorption partition coefficient based upon organic carbon content rather than total soil mass has been proposed by Lambert (1968) and Hamaker and Thompson (1971). Using this procedure, the amount of pesticide adsorbed was expressed as μg/g organic carbon and the Freundlick constant (K_{OC}) for each adsorption isotherm was computed. These values are also presented in Table 3. It is apparent that the values of K_{OC} for a given pesticide are much less variable (smaller percent CV) among the four soils studied than are the K values uncorrected for organic carbon. These results are in general agreement with the observations of Hamaker (1975) where the K_{OC} values for a given pesticide were nearly independent of soil type. It should be recognized, however, that other factors such as soil pH, clay content, and cation exchange capacity may also play a significant role in determining pesticide adsorption by soils (Bailey and White, 1970). On the basis of the K_{OC} values listed in Table 3, the extent of pesticide adsorption in soils was in the order of terbacil < trifluralin < 2,4-D amine < atrazine < methyl parathion.

Column Displacement Experiments

The partial differential equation generally assumed to describe the movement of pesticides and other adsorbed

TABLE 3. FREUNDLICH CONSTANTS CALCULATED FROM EQUILIBRIUM ADSORPTION ISOTHERMS FOR VARIOUS SOIL-PESTICIDE COMBINATIONS

PESTICIDE	SOIL	K_M[†]	K_G[‡]	N	K_{OC}[‡‡]
Atrazine	Webster	9.12	6.03	0.73	155.8
	Cecil	0.84	0.89	1.04	98.9
	Glendale	0.69	0.62	0.93	124.0
	Eustis	0.85	0.62	0.79	110.7
	Average ± % CV*	2.87 ± 145	2.04 ± 131	0.87 ± 16	122.3 ± 20
Methyl Parathion	Webster	18.67	13.39	0.75	346.0
	Cecil	4.81	3.95	0.85	438.6
	Glendale	6.05	3.57	0.61	714.5
	Eustis	3.30	2.72	0.86	486.4
	Average ± % CV	8.21 ± 86	5.91 ± 85	0.77 ± 15	496.4 ± 32
Terbacil	Webster	2.96	2.46	0.88	63.6
	Cecil	0.39	0.38	0.99	42.2
	Glendale	0.42	0.38	0.93	76.0
	Eustis	0.15	0.12	0.88	21.4
	Average ± % CV	0.98 ± 135	0.83 ± 130	0.92 ± 6	50.8 ± 47
Trifluralin	Webster	2.49	2.93	1.15	75.7
	Cecil	0.43	0.46	1.05	50.7
	Glendale	1.31	1.60	1.18	177.8
	Eustis	0.23	0.24	1.06	43.2
	Average ± % CV	1.11 ± 92	1.31 ± 94	1.11 ± 6	86.8 ± 72
2,4-D Amine	Webster	7.27	4.62	0.70	119.4
	Cecil	0.84	0.65	0.83	72.2
	Glendale	--	--	--	--
	Eustis	1.14	0.76	0.73	135.7
	Average ± % CV	3.08 ± 118	2.01 ± 112	0.75 ± 9	109.1 ± 30

[†] K_M Freundlich constant when solution and adsorbed phase concentrations are expressed as μM/l and μM/kg of soil.

[‡] K_G Freundlich constant for solution and adsorbed phase concentrations are as μg/ml and μg/g of soil [$K_G = K_M(MW/1,000)^{1-N}$], where MW is the pesticide's molecular weight.

[‡‡] K_{OC} Freundlich constant for solution and adsorbed phase expressed as μg/ml and μg/g of organic carbon.

*CV is the coefficient of variation, % CV = (standard deviation/average) x 100.

solutes through soils under steady-state water flow conditions is (Van Genuchten, et al., 1974):

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \frac{\rho}{\theta}\frac{\partial S}{\partial t} \qquad [1]$$

where t is time (days), D is dispersion coefficient (cm^2/day), x is distance (cm), v is average pore-water velocity (cm/day), ρ is soil bulk density (g/cm^3), θ is volumetric soil-water content (cm^3/cm^3), and C and S are solution and adsorbed pesticide phase (μg/ml and μg/g), respectively. When the adsorption isotherm obeys the Freundlich equation, the convective-dispersive solute transport model (Equation 1) reduces to:

$$R(C)\,\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2} - v\,\frac{\partial C}{\partial x} \qquad [2]$$

where,

$$R(C) = [1 + \rho KNC^{N-1}/\theta] \qquad [3]$$

The retardation term R(C) is a quantitative index of the pesticide's mobility in that its value is equal to the ratio of the positions of the adsorbed and nonadsorbed solute fronts in soil. The value of the adsorption coefficient K in Equation [3] for nonadsorbed solutes (e.g., chloride or ^3H_2O) is equal to zero; hence, R(C) = 1. For adsorbed solutes, R(C) is greater than one because the value of K is larger than zero. Thus, larger values of R(C) indicate reduced pesticide mobility in soils. It may be noted from Equation [3] that for the case of nonlinear adsorption isotherms ($N < 1$), the value of the retardation term increases with decreasing solution concentration C, while for a linear isotherm ($N = 1$), R(C) is independent of pesticide solution concentration. Thus, the mobility of pesticides and other adsorbed solutes through soils is directly influenced by the shape of the equilibrium adsorption isotherms.

Effluent breakthrough curves (BTC) were measured for 2,4-D amine at two input concentrations (C = 50 and 5,000 μg/ml) and tritiated water (^3H_2O) using columns of each soil. Tritiated water represents a nonadsorbed solute and serves as a reference for the adsorbed pesticides. A shift of the BTC for adsorbed solutes to the right of ^3H_2O BTC is due to an adsorption-induced retardation. The greater the righthand shift of the BTC, the greater the adsorption; thus, a decrease in mobility. It is apparent from the data presented in Figure 1 that the mobility of 2,4-D amine in the Webster soil was significantly increased as the input concentration (C_0) increased from 50 to 5,000 μg/ml. Note that for the 5,000 μg/ml input concentration, 2,4-D amine was nearly as mobile as was ^3H_2O. The effect of increased mobility at high concentration was more pronounced in the Webster soil than in the other soils. These column results are consistent with Equation [3] and the measured nonlinear adsorption isotherms (Table 3) for 2,4-D amine. Similar results were obtained for other soil-pesticide combinations (Rao and Davidson, 1979).

The position of the BTC for an adsorbed solute is governed by the nature of the equilibrium adsorption isotherm (Equation 3), whereas the shape of the BTC (i.e., symmetry or lack of it) is defined by nonlinearity of the adsorption isotherm and the kinetics of adsorption-desorption processes. Symmetrical BTC are obtained when adsorption is an instantaneous process and the adsorption isotherm is linear. For nonequilibrium adsorption conditions during flow, asymmetrical BTC are generally obtained (Van Genuchten, et al., 1974; Rao, et al., 1979). All of the pesticide BTC measured in this study were asymmetrical in shape with extensive "tailing" observed as C/C_0 approached 1.0 or zero. Tailing was absent in ^3H_2O breakthrough curves. The extent of the asymmetrical shape of each pesticide BTC exceeded that which could be attributed to the nonlinear nature of the adsorption isotherms. Hence, much of the asymmetry measured for the pesticide BTC may be attributed to nonequilibrium conditions which exist in the soil columns during flow. Rao et al. (1979) presented an evaluation of two conceptual models where nonequilibrium during flow was attributed to either kinetics-controlled or diffusion-controlled adsorption-desorption processes.

The illustrated increase in pesticide mobility at high concentrations limits the usefulness of the present low concentration data base for developing safe management practices for pesticide disposal in the soil. However, underestimation of pesticide movement by assuming linear adsorption isotherms may not be severe for pesticides with low aqueous solubilities. Ou et al. (1978) showed that for high loading rates, up to 20,000 μg 2,4-D/g soils, there was a significant decrease in the pesticide degradation rate with a comcomitant depression of total microbial activity in the soil. Thus, due to rapid leaching and minimal microbial decomposition of pesticides at high concentrations, the potential for groundwater contamination with pesticides is increased.

Infiltration Experiments

Pesticide transport in soils during transient, unsaturated, and one-dimensional water flow was investigated using hand packed horizontal soil columns. In order to simulate a waste disposal site, the top

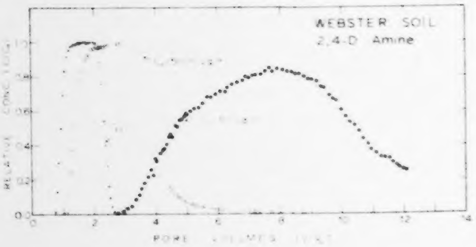

Figure 1. Effluent breakthrough curves for 2,4-D amine (C_0 = 50 and 5,000 μg/ml) and for tritiated water displacement through Webster soil column.

1.5 cm of each soil column was packed with pesticide-treated soil (2,000 μg pesticide/g soil), and 0.01 N $CaCl_2$ was infiltrated into the soil at a constant negative head (-4 cm of water). During infiltration, the rate of wetting front advance was recorded by visual observations. The soil column was cut into 1-cm segments at the end of the infiltration. In each soil segment, the total amount of pesticide (sum of solution, adsorbed, and solid phases) was determined by combustion, while the soil-water content was measured by oven-drying.

The depth (χ_p) to which the pesticide front moved in a soil due to water infiltration was dependent upon the wetting front depth (χ_w), the pesticide adsorption isotherm constants (K and N), and the aqueous solubility (C_s) of the pesticide. The relationship between these variables may be expressed as:

$$\frac{\chi_w}{\chi_p} \simeq 1 + \frac{\rho K C_s^{N-1}}{\bar{\theta}} \qquad [4]$$

where, ρ is the soil bulk density (g/cm^3) and $\bar{\theta}$ is the average soil-water content (cm^3/cm^3) in the wetted zone behind the wetting front. It should be noted that for the case of a linear adsorption isotherm (N = 1), Equation 4 is exact and the retardation of the pesticide front due to adsorption is independent of concentration, while for the nonlinear isotherm case, Equation 4 is only an approximation.

Assuming that Darcy's law is valid for unsaturated water flow in soils, the rate of the advance of the wetting front is given by (Kirkham and Powers, 1972):

$$\chi_w = mt^{1/2} \qquad [5]$$

where, m is a constant and t is time (min). In the present study, Equation [5] described ($r^2 \geq 0.95$) the advance of the wetting front for all soil columns considered. The values of m and other pertinent data for the inflitration experiments are summarized in Table 4.

Measured pesticide concentration profiles and soil-water content distributions at the end of infiltration in Eustis, Cecil, and Webster soil columns are shown in Figures 2 and 3. Because the final wetting front position in each soil column was different, for ease of comparison the ordinate in Figures 2 and 3 is plotted as soil depth relative to the wetting front depth (i.e., χ/χ_w). Except for the 2,4-D-Eustis and the terbicil-Eustis data, the relative mobilities of the pesticides are in general agreement with those anticipated from the equilibrium adsorption isotherms and pesticide aqueous solubilities. The measured mobility of terbacil and 2,4-D in the Eustis soil (Figure 2) was nearly the same although the adsorption coefficient for 2,4-D is greater than that for terbacil in Eustis soil (see Tables 3 and 4). The importance of aqueous solubility is demonstrated by the atrazine data in the Eustis soil (Figure 2 and Table 4). Note that the volume of water infiltrated into the soil column could solubilize and transport only about 4% of the total pesticide present in the top 1.5 cm segment; thus, most of the atrazine does not appear to have moved. The retardation factors, (χ_w/χ_p), calculated by Equation [4] are generally larger than those measured in the infiltration experiments (Table 4). Similar results were reported by Wood and Davidson (1975) for transient-flow studies and by Davidson and Chang (1972) for saturated flow experiments. The kinetics of pesticide adsorption-desorption in soils are not understood well enough at this time (Rao et al., 1979) to describe modeling the nonequilibrium conditions for pesticide

TABLE 4. PHYSICAL DATA FOR INFILTRATION EXPERIMENTS

SOIL	PESTICIDE	C_s (μg/ml)	ρ (g/cm^3)	X_w (cm)	m* (cm/min$^{1/2}$)	X_w/X_p Measured	X_w/X_p Calculated**	Volume of water applied (ml)	Pesticide Recovery (%)
Eustis	Atrazine	33	1.67	21.3	3.195	2.50	3.03	44	>100
Eustis	2,4-D	650	1.69	30.0	3.854	1.05	1.89	68	>100
Eustis	Terbacil	710	1.64	29.5	4.039	1.11	1.37	63	91
Cecil	Terbacil	710	1.51	28.4	0.705	1.49	3.03	68	93
Webster	Terbacil	710	1.40	24.1	0.543	4.16	4.55	67	99

* see Equation [5]
**see Equation [4]

adsorption-desorption during transient soil-water flow. Additional studies are needed in this area.

Pesticide Degradation

Total CO_2 evolution (respiration) is generally a good indicator of soil microbial activity. This procedure was used by Stojanovic et al. (1972) to estimate pesticide degradation rates in soil systems receiving large pesticide concentrations. A more direct procedure for determining pesticide degradation, however, is to measure $^{14}CO_2$ evolution from uniformly ring-labeled ($^{14}CF_3$ position for trifluralin) pesticides.

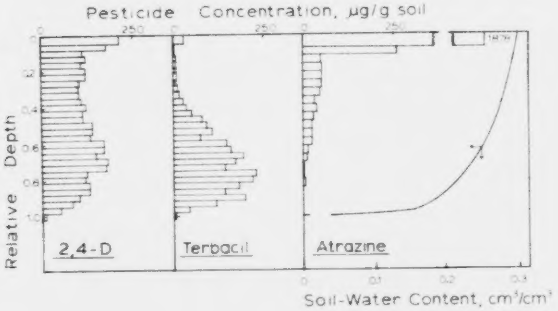

Figure 2. Soil-water content (solid line) and 2,4-D, terbacil and atrazine concentration distribution in Eustis soil following infiltration of water to approximately 30-cm. Soil was initially air dry and herbicide was in top 1.5 cm of soil (2,000 μg/g of soil).

Because 2,4-D degradation was determined by measuring the evolution of $^{14}CO_2$

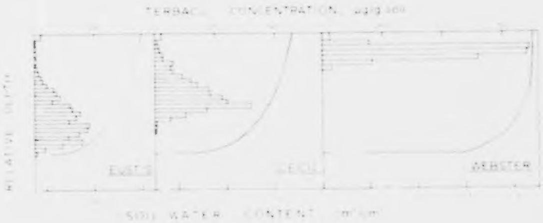

Figure 3. Soil-water content (solid lines) and terbacil concentration distributions in Eustis, Cecil and Webster soils following infiltration of water to approximately 30-cm. Soils were initially air dry and herbicide was in top 1.5-cm of soil (2,000 μg/g of soil).

from uniformly ring-labeled material, it can be assumed that the 2,4-D was degraded to its final oxidation products, CO_2, H_2O, and Cl^-. At concentrations of 50 and 500 ppm in the Webster silty clay loam, both forms (technical grade and formulated) of 2,4-D were mineralized rapidly to CO_2, H_2O, and Cl^- within 40 days of incubation. At 5,000 ppm, both forms were degraded, but exhibited lag periods of 10 to 19 days for the technical and formulated 2,4-D material, respectively. No significant degradation occurred before 50 days for 20,000 ppm, and a total of 11.5% and 21.5% of the technical grade and formulated material were degraded after 80 days of incubation (Ou et al. 1978a,b).

Unlike the Webster soil, total CO_2 evolution was inhibited in the Cecil soil which received 5,000 and 20,000 ppm of technical grade 2,4-D as well as 20,000 ppm of formulated 2,4-D. Small stimulations were noted in the total CO_2 evolution from the soil treated with 5,000 ppm of formulated 2,4-D. In contrast to the Webster soil, very little degradation was observed in the Cecil soil receiving 5,000 and 20,000 ppm. At a rate of 500 ppm, both forms of 2,4-D were degraded slowly. Only 10.5% and 6.3% of the technical and formulated material were degraded, respectively, in the Cecil soil after 80 days of incubation.

Attempts were made to stimulate 2,4-D degradation in the Cecil soil receiving 5,000 ppm of 2,4-D. In addition to 2,4-D (technical grade or formulated) and ^{14}C-2,4-D, the Cecil soil was amended with various nutrient sources. Readily degradable nutrients such as yeast extract (1%) and glucose (1%) plus urea (0.5%) did not stimulate 2,4-D degradation. Only a small stimulation, if any, occurred with these treatments with the exception of the treatment with lime plus 2,4-D degrading bacterium (Ou et al. 1978a,b). In this treatment 28.6 and 3.9% of the formulated and technical grade 2,4-D, respectively, were degraded in 60 days.

Both technical grade and formulated parathion at 25 ppm were degraded rapidly to CO_2 in the Webster and Cecil soils as indicated by $^{14}CO_2$ evolution from uniformly ring labeled ^{14}C-methyl parathion. More than half of the ^{14}C-methyl parathion in each soil was mineralized to $^{14}CO_2$ after 10 days of aerobic incubation. At the end of the 32-day incubation period, 75 to 79% of the ^{14}C-methyl parathion in the 25 ppm treatments was mineralized to $^{14}CO_2$. Of the total ^{14}C-activity added to the Webster and Cecil soil receiving 25 ppm of technical grade methyl parathion, 21 and 23%, respectively, could not be extracted by the organic solvent mixture methanol-acetone-benzene (1:1:1) and were termed "bound residues." Similar results have been reported by Lichtenstein, et al. (1977).

When the methyl parathion concentration was 10,000 ppm, less than 0.1% of ^{14}C-methyl parathion was mineralized to $^{14}CO_2$ in 52 days. These findings were supported by the fact that nearly 100% of ^{14}C-activity was extracted from each 10,000 ppm treated soil by the organic solvent mixture. Total CO_2 evolution in the 10,000 ppm treatments was reduced. The ^{14}C-activity remaining in the Webster and Cecil soil receiving 10,000 ppm of technical grade methyl parathion was 0.2 and 0.1%, respectively, after extraction with the organic solvent mixture at the end of the incubation period.

Atrazine and trifluralin at an application rate of 10 ppm were mineralized slowly in the Webster and Cecil soil. No more than 5% of ^{14}C-atrazine or ^{14}C-trifluralin was mineralized to $^{14}CO_2$ in the 10 ppm treatments after 80 days of aerobic incubation. Less than 0.1% of ^{14}C-activity in the 10,000 ppm treatments was mineralized to $^{14}CO_2$. Unlike 2,4-D and methyl parathion, microbial activity in soils generally was not affected by the addition of 10,000 ppm of atrazine or trifluralin.

Metabolites and Bound Residues

Only tentative identifications of atrazine metabolites were made. Structures are based on thin layer and gas chromatographic behavior. In the Webster soil treated with 10 or 1,000 ppm, 4 to 8 percent of the radioactivity was associated with a compound or compounds having a relative R_f similar to that of 2-chloro-4-amino-6-isopropylamino-s-triazine (0.80) and/or 2-chloro-4-ethyl-amino-6-amino-s-triazine (0.88). One to four percent of the activity was associated with a component having a relative R_f indistinguishable from that of 2-hydroxy-4-ethylamino-6-isopropylamino-s-triazine (0.48;

hydroxy-atrazine). Less than 2 percent of the radioactivity was detected at a relative R_f similar to that of 2-hydroxy-4-amino-6-isopropyl-amino-s-triazine (0.10) and 2-hydroxy-4-ethylamino-6-amino-s-triazine (0.10). In the Cecil soil, all the radioactivity not associated with atrazine had a relative R_f corresponding to hydroxy-atrazine (0.48). Percentages of metabolites increased with time and corresponded to a reduction in the level of the parent compound.

The percentage of unextractable radioactivity was generally higher at 10 and 1,000 ppm for the Cecil soil than for the Webster soil; this difference was not observed at the 20,000 ppm treatment. There was no apparent difference in bound residues between the technical and formulated applications at any of the three concentrations studied. The percentage of bound ^{14}C-activity increased with time and as much as 30% of the ^{14}C detected in the soil was unextractable. In addition to the trifluralin added to the Webster and Cecil soils, four compounds were identified: (1) α,α,α-trifluoro-2,6-dinitro-N-propyl-p-toluidine, (2) α,α,α-trifluoro-2,6-dinitro-p-toluidine, (3) 2-ethyl-7-nitro-1-propyl-5-trifluoromethyl benzimidazole, and (4) 2-ethyl-7-nitro-5-trifluoromethyl benzimidazole. Each compound identified was identical to authentic standards in chromatographic behavior and mass spectral fragmentation patterns. In addition to the four metabolites described above, two other unknown compounds were detected (Wheeler et al., 1979).

No differences in metabolic rates or pathways could be detected between the Webster or Cecil soils or between the formulated or technical trifluralin. The percentage bound was calculated by measuring the organic solvent extractable ^{14}Carbon and the unextractable amount as determined by combustion of the soil after extraction. For the 10 ppm concentration, a greater percentage of technical trifluralin was bound to Webster soil than to Cecil. Ten days after application, 10% was bound and by 35 days it had risen to 30% and after 65 days of incubation, 72% was unextractable. The quantity of formulated trifluralin bound in the Webster soil was only measured after 68 and 84 days incubation, but showed a similar but somewhat lesser (45 and 51%) amount of bound residue than that measured for the technical material.

Recent reports by Katan et al. (1976) and Katan and Lichtenstein (1977) show rapid binding of the parathion amine analogue which suggests that a similar phenomenon may have occurred with trifluralin in the Webster soil. The parent compound represented 90% or more of the extractable ^{14}C, while considerable radioactivity was not extracted. Thus, it is possible that some metabolic products were formed and a substantial portion of them were bound. This would explain why certain previously reported metabolites were not detected in the extract or were only found in small quantities. In an effort to examine this possibility, trifluralin, mono-dealkylated, and di-dealkylated derivatives were incubated in sterilized Webster soil for four hours. Percentages of each compound extractable after four hours were 89, 75 and 57 for the above compounds, respectively. Thus, in the Webster soil there was a clear relationship between the amount of non-extractable material and the substitution on the amino nitrogen. This is consistent with the findings of Katan and Lichtenstein (1977) with amino analogs of parathion. If one fortifies Webster soil with either trifluralin or the di-dealkylated derivative and immediately perform an extraction, 93-95% of both compounds were recoverable. Substantial binding did not occur for the di-dealkylated derivative in the sandy Cecil soil. Thus, it is possible in the case of the Webster soil, that metabolites containing secondary or primary amino functional groups became a part of the "bound" portion of the residue. The absence of the same magnitude of binding in Cecil soil could be the result of different kinds and numbers of microbial populations, etc. This could also influence the formation of microbially induced amino metabolites in the Cecil soil.

In the majority of cases, parent 2,4-D was the only radioactive component isolated from the soil. In a few cases, 2,4-dichlorophenol (based upon thin-layer chromatography) was detected. It appeared that more 2,4-dichlorophenol accumulated at the 500 ppm concentration after 7 to 10 days of incubation than for other concentrations and was present to a greater extent in the Webster than in the Cecil soil. Only the parent 2,4-D, however, was detected after 29 days of incubation.

IMPLICATIONS OF PROJECT RESULTS WITH REGARDS TO PESTICIDE DISPOSAL

Two significant conclusions can be made regarding the adsorption results obtained during this project. First, the Freundlich adsorption equation described all pesticide adsorption isotherms considered for solution concentrations up to the aqueous solubility of the pesticide. Thus, the pesticide adsorption sites for all soils investigated were apparently not saturated at any concentration considered in this study. Second, contrary to a frequent assumption, pesticide adsorption isotherms were not linear, that is, N in the Freundlich equation was generally less than one. The nonlinearity of the pesticide adsorption isotherm is an important observation because it explicitly points out that pesticides will be more mobile in soils containing pesticide concentrations similar to those associated with pesticide waste disposal sites. This is especially true for pesticides that are very soluble in water (e.g., 2,4-D amine).

The increased pesticide mobility at high pesticide concentrations limits the usefulness of the available low concentration data base for developing "safe" management practices for pesticide disposal procedures in soils. If a linear adsorption isotherm is assumed on the basis of the low pesticide concentration data, one underestimates the soil depth to which a pesticide will leach or move for a given water input. The seriousness of the failure of the low concentration data base to describe the true mobility of a pesticide as it moves toward the groundwater from a waste disposal site depends upon the water solubility of the pesticide and nonlinearity of the adsorption isotherm. For example, the adsorption isotherms for atrazine and 2,4-D and a Eustis soil were similar (see Table 3); however, 2,4-D moved similar to an unadsorbed chemical as it moved away from a simulated waste disposal site, while the mobility of the atrazine through the same soil was about 2.5 times less. To have assumed that the adsorption isotherms were linear would have resulted in a serious underestimation of the depth to which each pesticide would have moved for a given water input.

Many of the pesticides available on the market today are biodegradable in soils when applied at low concentrations (0.5 to 10 kg/ha). However, many of these same organic chemicals become persistant when applied to soils at high concentrations. It has been observed that some soils are able to biologically mineralize one pesticide (e.g., 2,4-D in Webster soil), but the same pesticide may be persistant in another soil (e.g., Cecil). This study clearly points out that the soil respiration rate of a soil receiving high pesticide concentrations is not, in general, a reasonable procedure for measuring pesticide degradation potential. Also, the apparent persistance of some pesticides may be further confounded by the formation of metabolites which are "bound" (not extractable by recommended procedures) to the soil and suggest a greater apparent loss of the original chemical than what actually occurred.

The contrast between the behavior of soil environments containing large and small pesticide concentrations illustrates the importance and potential for management of pesticide waste disposal sites. Many soils frequently can be altered chemically and/or biologically to enhance their potential for biologically degrading pesticides. Also, microorganisms capable of degrading specific chemicals at high concentrations have been identified and isolated which could be added to a waste disposal site to enhance the degradation and mineralization of a given chemical. Because of increased pesticide mobility at high concentrations, the chemical may not, however, remain in the vicinity of desired biological environment for degradation; thus, it is important to manage both the water leaching rate and biological environment for optimum inactivation and efficiency of a pesticide waste disposal site.

A major limitation in using the results of this project is that only one chemical was applied to a soil at a time. Combinations or mixtures of pesticides would be the common situation for a pesticide waste disposal site. Waste disposal sites receiving several pesticides may fail to function as designed for a specific pesticide because of interactions between chemicals and their environment. The behavior of a pesticide mixture may or may not be independent or additive, but rather based upon the influence of one pesticide and/or the formulation associated with a given pesticide. Problems which may arise owing to the mixing of pesticides in a waste disposal site should be considered before site selection and management protocols are defined by the United States Environmental Protection Agency. This work should include the evaluation of the major surfactants used with pesticides and various formulation chemicals.

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INFLUENCE OF LEACHATE QUALITY ON SOIL ATTENUATION OF METALS

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ABSTRACT

The rate of movement through soil of constituents in waste leachates, whether from municipal solid waste (MSW) or industrial wastes depends on the nature of: (a) the porous medium through which solutions move (soil, geologic debris, clays, etc.), (b) the vehicle transporting the constituent (leachate), and (c) the potential pollutant constituent itself (Cd, Fe, Ni and Zn). This presentation is concerned with the rate of movement of Cd, Fe, Ni, and Zn as correlated with certain measurable broad parameters of MSW landfill leachates. The most prominent, readily measurable parameters have been identified as total organic carbon (TOC), pH, concentration of soluble common salts, and iron (Fe). The influence of these parameters on the prediction of movement of Cd, Fe, Ni, and Zn through soils is discussed and quantitative data on rate of movement presented.

BACKGROUND

The establishment of mathematical equations for predicting movement of metals through soil and geologic debris depends on the identification and quantification of certain major components of the land disposal environment, Fuller et al.(1979a,b,c), Alesii et al.(1978), and O'Donnell et al. (1977). The major components are (a) the soil and geologic debris, (b) the leachate and (c) the polluting constituent, Fuller (1977) and Fuller et al.(1979a,b). The effect of the most influential soil factors on movement of heavy metals has been well researched and reported earlier, Korte et al. (1976, 1975), Fuller (1977), Fuller (1978), O'Donnell et al.(1977). However quantitative data for specific potential polluting constituents is needed. The purpose of the research presented here, therefore, is to extend the original soil formula as a user-oriented predictive tool to include quantitative data on prominent, readily measurable MSW leachate characteristics. The cadmium (Cd) prototype, presented in our report last year, Fuller et al. (1979c), forms a base to accomplish this purpose for nickel (Ni), zinc (Zn) and to a lesser extent iron (Fe).

The suggested major MSW leachate properties affecting metal attenuation to be quantified are (a) total organic carbon (TOC), total soluble inorganic salts (salt), and iron (Fe). Predictions for metal movement then are to be based on regression analyses because models based on chemical reactions have rarely been successful.

OBJECTIVES

The objectives, therefore, were to (a) evaluate the effects of passing MSW leachate through representative soil on the attenuation of Cd, Fe, Ni, and Zn contained in the leachate, and (b) relate attenuation of the metals to specific parameters useful for establishment of a field-oriented predictive tool.

MATERIAL

Six soils were perfused with MSW leachate enriched singly with Cd, Ni, and Zn at a concentration of 100 ppm metal. Some soil properties are reported in Table 1 and leachates in Table 2. These soils have been more fully characterized by Fuller (1978). They range in pH from 4.2 to 7.8 and clay percentages 1 to 52. The soils were packed into 10-cm lengths of 5-cm PVC pipe at known and reproduceable bulk densities.

TABLE 1. SOILS USED IN THE Cd, Fe, Ni, AND Zn ATTENUATION RESEARCH

Soil Series*	Soil Order	Clay	Silt	Sand	Soil Paste pH	Cation Exch. Capacity meq/100g	Elec. Cond. of Extract µmhos/cm³	Column Bulk Density g/cm³	Soil Surface Area m²/g	Predominant Clay Minerals†
Davidson	Ultisol	52	23	25	6.4	9	169	1.40	51.3	Kaolinite
Molokai	Oxisol	52	25	23	6.2	14	1262	1.44	67.3	Kaolinite, gibbsite
Nicholson	Alfisol	49	47	3	6.7	37	176	1.53	120.5	Vermiculite
Fanno	Alfisol	46	19	35	7.0	33	392	1.48	122.1	Montmorillonite, mica
Mohave(Ca)	Aridisol	40	28	32	7.8	12	510	1.54	127.5	Mica, montmorillonite
Chalmers	Mollisol	31	52	13	6.6	22	288	1.60	95.6	Montmorillonite, vermiculite
Ava	Alfisol	31	60	10	4.5	19	157	1.45	61.5	Vermiculite, kaolinite
Anthony	Entisol	15	14	71	7.8	10	328	1.87	49.8	Montmorillonite, mica
Mohave	Aridisol	11	37	52	7.3	10	615	1.78	38.3	Mica, kaolinite
Kalkaska	Spodosol	5	4	91	4.7	6	237	1.53	8.9	Chlorite, kaolinite
Wagram	Ultisol	4	8	88	4.2	2	225	1.89	8.0	Kaolinite, chlorite
River alluvium	Entisol	1	2	97	7.2	2	210	1.73	3.6	Kaolinite, mica

*Oriented on basis of clay content

†Listed in order of importance

TABLE 2
MUNICIPAL SOLID WASTE LEACHATE II CHARACTERISTICS

Constituent	Concentration
pH	6.9
Electrical Conductivity (EC) mmhos/cm	5.1
Total Organic Carbon (TOC) - ppm	2000
Calcium - ppm	91
Magnesium - ppm	35
Potassium - ppm	653
Iron - ppm	39
Manganese - ppm	0.10
Phosphorus - ppm	1.00
Silicon - ppm	21.00
Zinc - ppm	0.46

MSW leachates were enriched to contain ∿ 100 ppm Cd, Ni, or Zn. Iron was evaluated as a natural constituent, not enriched. Total organic carbon (TOC) effects were compared by using undiluted (100%), and water-diluted (10, 25, and 50% original) leachates. Each dilution was also brought to levels of approximately 2,000, 1,000, and 500 ppm of representative salts to evaluate the salt effect on Cd, Ni, and Zn migration. Various salt levels were developed by adding $CaCl_2$, $Mg(NO_3)_2$, NaCl, and KCl to give the desired concentration at the same cation ratio as the natural landfill leachate used. The treatments appear in Table 3. Treatment of ∿ 500 ppm salt and 100% leachate was not made since the natural leachate contained more than 500 ppm inorganic salt.

METHODS

MSW leachate was displaced through the soil under saturated-anaerobic conditions similar to that found for most landfills. The fluxes ranged between 3 to 11 cm/day as controlled by a peristaltic pump. Effluent displacements were collected in a fraction collector initially every 2 or 3 hours depending on the rate of migration of metal. Both influent and effluent were analyzed for the metal in question on a daily basis. The initial leachate was lowered to a pH of 5.2 before metal enrichment, aqueous dilution and inorganic salt addition. The pH of the leachate used in this study ranged between 5.2-5.4.

The soil influent and effluent MSW leachate was monitored for TOC, Ca, Mg, Na and K according to standard atomic absorption procedures previously described (Korte et al., 1976). The Cd, Fe, Ni, and Zn, trace and heavy metals of the leachates were determined by atomic absorption spectrophotometry according to the U.S. EPA Standard Procedure (EPA 1974 and 1979).

RESULTS

Iron

The influence of MSW leachate constituents on the movement of indigenous Fe through Kalkaska sand is illustrated in Figure 1 to be significant. Natural Fe of MSW Leachate II moved through soil[1] in direct proportion to the TOC, salts, and iron concentration where levels of these constituents ranged from 3,700-210, 10,000-2,000, and 1,000-100 mg/ℓ, respectively. One can only speculate as to the reason for these trends. For example, well known sequestering constituents, such as fulvic and humic acids, are included in the broad category of TOC. Greater the concentration of these compounds, the greater is the opportunity for more rapid migration through soil. Also, there must be a common mass ion effect with such high concentrations of inorganic salts. Therefore, one may expect a greater rate of migration to be associated with the greater concentration or mass of ions in solution. The iron effect is not clear but one may expect there to be a competitive effect for adsorption or retention soil surface sites the greater the concentration of soluble Fe in the leachate.

Cadmium

The same trend for attenuation of leachate Fe in soil to be significantly influenced by TOC, salts, and iron is exhibited with Cd, Figure 2. The higher the concentration of these three constituents, the higher was the rate of migration through Ava silty clay soil. Again, specific mechanisms of attenuation are not identified. Nevertheless, broad parameters such as these may be sufficiently sharp to be useful tools in model development for prediction of heavy metal migration rates.

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[1] Soils other than Kalkaska sand not shown because of the space problem associated with the great volume of data.

TABLE 3

CONCENTRATION OF INORGANIC SALTS, TOTAL ORGANIC CARBON, Ni AND Zn IN THE VARIOUS DILUTED EXPERIMENTAL MSW LEACHATES

Leachate No.	Ni or Zn ppm	Salts ppm	TOC ppm	Leachate Dilution %
		Ni-Enriched Leachate		
1	100	2012	1953	100
2	105	935	2104	100
3	102	2094	1188	50
4	105	994	1284	50
5	102	600	1142	50
6	102	2353	591	25
7	105	800	552	25
8	102	385	532	25
		Zn-Enriched Leachate		
1	105	1992	2508	100
2	105	1043	2621	100
3	100	1943	1438	50
4	100	977	1370	50
5	100	596	1065	50
6	98	1994	170	10
7	97	1094	192	10
8	100	568	216	10

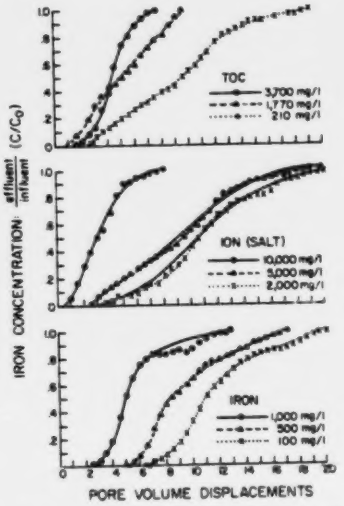

Figure 1. Effect of total organic carbon constituents, salt, and iron on the migration rate of Fe from Leachate II through Kalkaska soil.

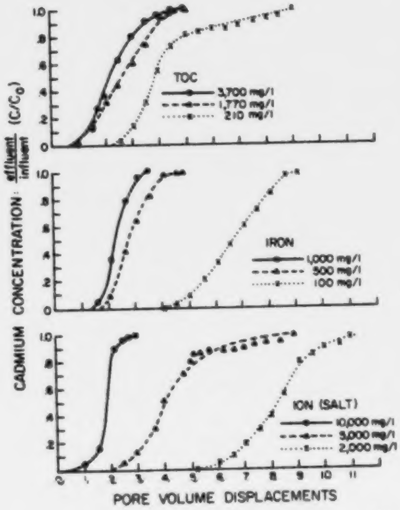

Figure 2. Effect of total organic carbon constituents, salt, and iron on the migration rate of Cd from Leachate II through Ava silty clay.

Nickel

As illustrated in Figures 3 and 4 both, the quantity of organic constituents (TOC) and common inorganic salt (ION) in the MSW leachate significantly influenced the rate of Ni movement through the soils.[1] The higher the concentration of these constituents, the higher was the rate of movement and the lower was the Ni attenuation through the soils. Reducing the TOC to ∿ 50 and 10% of the original leachate levels proportionately decreased rate of movement in the Ava silty clay, Figure 3. This effect was less pronounced in the Davidson clay, yet it was significant, Figure 4. The influence of salt concentration appeared to be more obvious with the Ava silty clay than the Davidson clay despite the lower clay content of the Ava soil. On the other hand, there is a greater surface area available for adsorption and other reactions to occur in the Ava (61.5 m^2/g, total soil surface area) than in the Davidson (51.3 m^2/g, total soil surface area) soil. The higher silt content of Ava silty clay (Ava 60%, Davidson 23%) more than compensated for the lower clay (< 2μ) content (Ava 31%, Davidson 52%). Furthermore, the higher hydrous oxides of the Davidson clay did not appear to fully compensate for the greater surface area of the Ava silty clay.

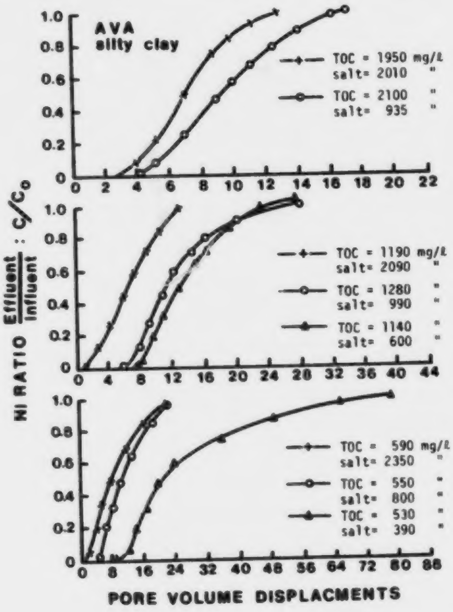

Figure 3. The influence of organic carbon (TOC) and salt (ION) concentration in MSW leachate on Ni movement through Ava sic.

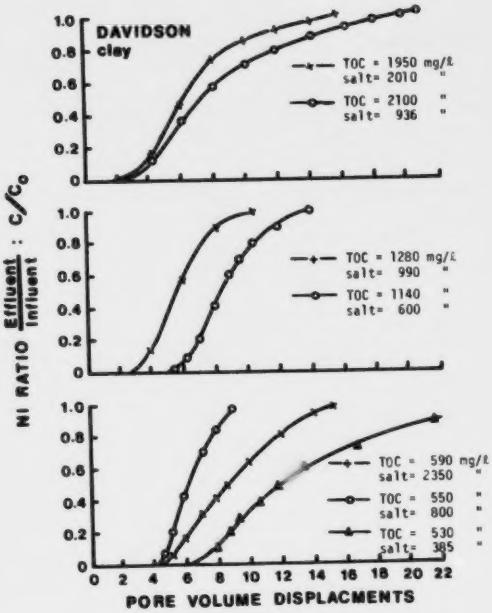

Figure 4. The influence of organic carbon (TOC) and salt (ION) concentration in MSW leachate on Ni movement through Davidson c.

The concentration effects of TOC and salt (ION) on the quantity of Ni retained per unit weight of soil at Breakthrough ($C/C_0 = 1.0$) are also indicated in Table 4. The lower the level of these constituents, the lower was the rate of metal migration through the six soils. Particle size distribution and surface area effects are indicated to favor greater attenuation in the finer than coarser soils.

These effects of leachate quality are reflected further in Ni migration velocity through soils as reported for Davidson clay, Ava silty clay, and Wagram sand in Table 5. Sands that are very low in clay such as the Wagram s do not always conform to the patterns of silty and clayey soils. This is due primarily to the very rapid movement of the leachates through the soils and the very low retention of heavy metal contributing to a large error factor in measurements.

Zinc

Zinc reacted to different concentrations of organic carbon (TOC) and inorganic

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[1] Data for other soils not shown due to need for economy of space.

TABLE 4

AMOUNT OF MSW LEACHATE II PASSED THROUGH SOIL COLUMNS AND QUANTITY OF NICKEL RETAINED PER GRAM OF SOIL AT BREAKTHROUGH

Soil	100% MSW Leachate II				50% MSW Leachate II						25% Leachate II					
	1*		2		3		4		5		6		7		8	
	Amt. ml	Ret. μg/g	Amt. ml	Ret. μg/g	Amt. ml	Ret. μg/g	Amt. ml	Ret. μg/g	Amt. ml	Ret. μg/g	Amt. ml	Ret. μg/g	Amt. ml	Ret. μg/g	Amt. ml	Ret. μg/g
Davidson	2047	304	1583	261	1014	199	1274	338	1072	300	824	184	1561	294	5216	640
Chalmers	1954	402	2525	571	4411	551	3276	779	2940	874	4511	632	3423	996	7700	1366
Ava	1932	496	1647	334	1287	190	2779	429	3003	323	1907	344	4887	597	7818	753
Anthony	1152	195	1624	217	1145	200	1973	302	1612	258	1683	240	2205	244	5582	797
Kalkaska	2098	180	1437	139	1460	130	1937	259	1779	259	1464	195	1231	124	2929	395
Wagram	658	65	671	38	420	36	1488	90	452	48	2218	135	494	32	808	43

*Refers to Leachate II composition of salt, TOC, and Ni as related to MSW Leachate II dilution recorded in Table 4.

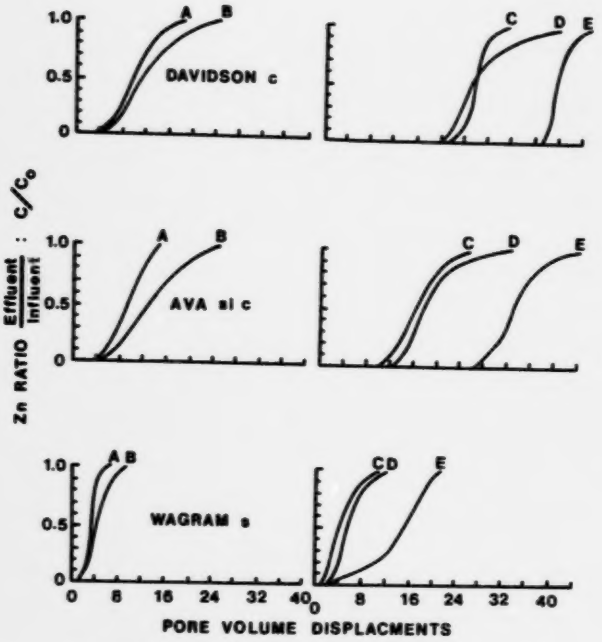
TABLE 5

THE VELOCITY OF NICKEL THROUGH THREE SOILS AS INFLUENCED BY MSW LEACHATE II AT VARIOUS TOTAL ORGANIC CARBON (TOC) AND SALT (ION) CONTENTS AT PORE WATER VELOCITY OF 10 cm/day.

Soil	Leachate %	Salt ppm	Velocity in cm/day if C/C_o equals ratio below:								
			.1	.2	.3	.4	.5	.6	.7	.8	.9
			velocity in cm/day								
Davidson clay	100	2000	1.33	1.26	1.22	1.18	1.15	1.13	1.10	1.09	1.08
		1000	1.50	1.44	1.40	1.37	1.34	1.30	1.26	1.20	1.12
	50	2000	2.00	1.91	1.85	1.81	1.77	1.73	1.69	1.64	1.59
		1000	1.17	1.13	1.12	1.12	1.12	1.12	1.12	1.13	1.15
		500	1.14	1.12	1.12	1.11	1.11	1.11	1.10	1.07	0.93
	10	2000	1.66	1.67	1.69	1.66	1.65	1.65	1.64	1.64	1.47
		1000	1.22	1.18	1.16	1.13	1.11	1.09	1.06	1.02	0.96
		500	0.90	0.89	0.88	0.87	0.87	0.85	0.80	0.70	0.64
Ava silty clay	100	2000	1.30	1.24	1.19	1.16	1.13	1.11	1.09	1.06	1.04
		1000	1.06	1.00	0.96	0.43	0.90	0.88	0.85	0.84	0.83
	50	2000	1.71	1.64	1.59	1.54	1.47	1.43	1.40	1.36	1.27
		1000	0.90	0.89	0.87	0.86	0.83	0.78	0.70	0.66	0.62
		500	0.69	0.68	0.68	0.67	0.67	0.67	0.65	0.57	0.49
	10	2000	1.13	1.07	1.03	0.95	0.91	0.90	0.88	0.78	0.76
		1000	0.91	0.90	0.89	0.88	0.87	0.87	0.85	0.77	0.65
		500	0.43	0.40	0.37	0.34	0.32	0.29	0.27	0.23	0.18
Wagram sand	100	2000	3.66	3.28	3.27	2.84	2.67	2.47	2.28	2.05	1.68
		1000	7.27	6.67	6.34	6.09	5.93	5.81	5.67	5.69	5.87
	50	2000	5.64	5.32	5.15	4.97	4.83	4.67	4.56	4.40	4.20
		1000	4.67	4.25	3.96	3.68	3.52	3.34	3.16	2.90	2.64
		500	4.29	4.03	3.83	3.67	3.54	3.41	3.28	3.14	2.94
	10	2000	5.67	5.36	5.16	5.01	4.89	4.77	4.64	4.52	4.34
		1000	6.18	5.82	5.60	5.42	5.26	5.11	4.97	4.80	4.58
		500	4.01	3.62	3.49	3.34	3.21	3.07	2.93	2.72	2.50

salts (ION) the same way as Ni despite the slower migration rate of Zn through the soil, Figure 5. At the lowest concentration of TOC ∿ 200 ppm, and salt ∿ 500 ppm in leachate, Zn moved several times more slowly through soils than at the highest concentration of ∿ 2,500 ppm TOC and 2,000 ppm salts.

Furthermore, calculation of the velocities of Zn at different ratios of effluent/influent or C/C_o concentrations according to the Lapidus and Amundson (1952) model, reveals and identifiable effect of different TOC and salt concentrations on Zn movement, Table 6.



A. ~ 2,000 mg/ℓ TOC + 2,000 mg/ℓ salts.
B. ~ 2,000 mg/ℓ TOC + 1,000 mg/ℓ salts
C. ~ 1,000 mg/ℓ TOC + 2000 mg/ℓ salts
D. ~ 1,000 mg/ℓ TOC + 1000 mg/ℓ salts
E. ~ 1,000 mg/ℓ TOC + 500 mg/ℓ salts

Figure 5. The influence of MSW leachate concentration of organic carbon (TOC) and inorganic salts (ION) on the movement and breakthrough of Zn through three soils.

TABLE 6
THE VELOCITY OF ZINC THROUGH THREE SOILS AS INFLUENCED BY MSW LEACHATE II AT VARIOUS TOTAL ORGANIC CARBON (TOC) AND SALT (ION) CONTENTS FOR PORE WATER VELOCITY EQUAL TO 10 cm/day

Soil	TOC ppm	Salt ppm	Velocity in cm/day if C/C_o equals ratio below: .1	.2	.3	.4	.5	.6	.7	.8	.9
			velocity in cm/day								
Davidson clay	2510	1990	1.13	1.07	1.02	0.97	0.94	0.90	0.85	0.79	0.68
	2620	1040	1.14	1.07	1.02	0.97	0.93	0.91	0.87	0.83	0.82
	970	1990	0.38	0.38	0.38	0.38	0.36	0.36	0.36	0.36	0.32
Ava silty clay	2510	1990	2.58	2.50	2.46	2.43	2.40	2.37	2.36	2.35	2.32
	2620	1040	1.13	1.05	0.99	0.97	0.89	0.85	0.80	0.76	0.70
	970	1990	0.41	0.38	0.32	0.29	0.28	0.25	0.24	0.21	0.18
Wagram sand	2510	1990	2.36	2.32	2.28	2.26	2.25	2.22	2.18	2.14	2.07
	2620	1040	2.33	2.75	2.27	2.60	2.62	2.94	2.57	2.57	2.57
	970	1990	2.38	2.24	2.15	2.08	2.04	1.98	1.94	1.91	1.89

DISCUSSION

Leachate Quality Effects

The purpose of obtaining quantitative information on leachate factors affecting metal attenuation is to aid in providing a suitable base for predicting attenuation in soils. One type example of our computations, involving the Lapidus and Amundson model is provided here. Cadmium is used as the prototype. All leachate factors, TOC, ION, and Fe, influenced migration rate of Cd through six different soils. The fastest rate of movement was associated with the highest concentration and the slowest rate associated with the lowest concentration. We (Fuller and Alesii, 1979 b) have earlier suggested that

1. At relatively low concentrations of inorganic salts and soluble Fe there is less competition for adsorption and other reactive sites on the surfaces of the soil particles than at high leachate constituent concentrations.

2. At relatively low concentrations of TOC there is less competition for ligand sites in the leachate but also there is less ligand available. The net effect on migration will be a complicated synergic relationship between the soil adsorption sites, the ligand, and competing ions in the leachate, and the metal under consideration.

3. Ferrous iron as well as organic molecules are active electron donors under anaerobic conditions and at the pH range involved.

PREDICTING METAL MOVEMENT

Table 7 gives the apparent Cd velocity through soils. To illustrate the application of these equations, suppose the soil and the leachate have the following properties:

1. Clay content = 21%
2. Free iron oxide = 1.2%
3. Soil porosity = 0.4
4. Total soluble ions in the leachate = 0.15%
5. Total organic carbon of the leachate = 0.6%
6. Concentrations of Cd in the leachate = 4 ppm.

Suppose the depth of ground water is 50 meters, the Cd concentration of ground water is zero and the Cd concentration limit for the ground water is 1.25 ppm. If the average infiltration is 1 cm/day, how long will it take for the ground water to reach the specified limit?

The pore water velocity is 1/0.4 = 2.5 cm/day and the relative concentration for Cd would be 1.25/4 = 3.1. Substitutions of the information into equation for $S_{.3}$ gives the velocity of Cd at 1.5 ppm concentration.

$$S_{.3} = [-.05(21)+.14(1.2)-.14(1.2)(.6+.15) + .05(21)(.6+.15)]2.5$$
$$S_{.3} = 1.025 \text{ cm/day}$$

TABLE 7
THE APPARENT Cd VELOCITY THROUGH THE SOIL MAY BE APPROXIMATED BY THE FOLLOWING SET OF EQUATIONS

$$S_{.1} = [\,-\,0.06 \times \text{clay} + 0.16 \times \text{FeO} - 0.16 \times \text{FeO} \times (\text{TOC} + \text{ION}) + 0.06 \times \text{clay} \times (\text{TOC} + \text{ION}) + 0.81] \times V$$

$$S_{.3} = [\,-\,0.05 \times \text{clay} + 0.14 \times \text{FeO} - 0.14 \times \text{FeO} \times (\text{TOC} + \text{ION}) + 0.05 \times \text{clay} \times (\text{TOC} + \text{ION}) + 0.63] \times V$$

$$S_{.5} = [\,-\,0.04 \times \text{clay} + 0.12 \times \text{FeO} - 0.12 \times \text{FeO} \times (\text{TOC} + \text{ION}) + 0.04 \times \text{clay} \times (\text{TOC} + \text{ION}) + 0.55] \times V$$

$$S_{.7} = [\,-\,0.03 \times \text{clay} + 0.11 \times \text{FeO} - 0.11 \times \text{FeO} \times (\text{TOC} + \text{ION}) + 0.03 \times \text{clay} \times (\text{TOC} + \text{ION}) + 0.48] \times V$$

$$S_{.9} = [\,-\,0.03 \times \text{clay} + 0.09 \times \text{FeO} - 0.11 \times \text{FeO} \times (\text{TOC} + \text{ION}) + 0.03 \times \text{clay} \times (\text{TOC} + \text{ION}) + 0.39] \times V$$

$$S_{.95} = [\,-\,0.03 \times \text{clay} + 0.09 \times \text{FeO} - 0.11 \times \text{FeO} \times (\text{TOC} + \text{ION}) + 0.03 \times \text{clay} \times (\text{TOC} + \text{ION}) + 0.36] \times V$$

where S_x represents the velocity of the relative concentration x.

Therefore, the time required for the concentration of 1.5 ppm to reach the 50 meter depth would be

50x100/1.025 = 4878 day = 13.4 years

It will take over 13.4 years for the concentration of Cd in the ground water to exceed 1.5 ppm limit.

The set of equations in Table 7 can also be used to obtain breakthrough curves at any depth within the profile. To do this, substitute the soil and leachate properties into the equations $S_{.1}$ through $S_{.95}$ and find the velocity of Cd movement for the relative concentrations (C/C_o) 0.1 through 0.95. Then, to find time, divide the desired depth to the velocity for each C/C_o and plot the time vs. C/C_o for that depth. Table 8 gives the velocity of Cd for each one of the relative concentrations of Cd for the soil and leachate described previously. In addition, the time required for each C/C_o to reach 50 and 80 meter depths are given. The breakthrough curves for the two depths are shown in Figure 6.

TABLE 8

VELOCITY VALUES FOR Cd AT GIVEN C/C_o AND THE TIME FOR WHICH THE C/C_o REACHES 50 AND 80 METER DEPTH

C/C_o		0.1	0.3	0.5	0.7	0.9	0.95
Velocity (cm/day)		1.36	1.03	.94	.82	.605	.503
Time (years) to reach a depth of:	50 meters	10.07	13.30	14.57	15.39	22.64	27.23
	80 meters	16.12	21.28	23.32	24.63	36.23	43.57

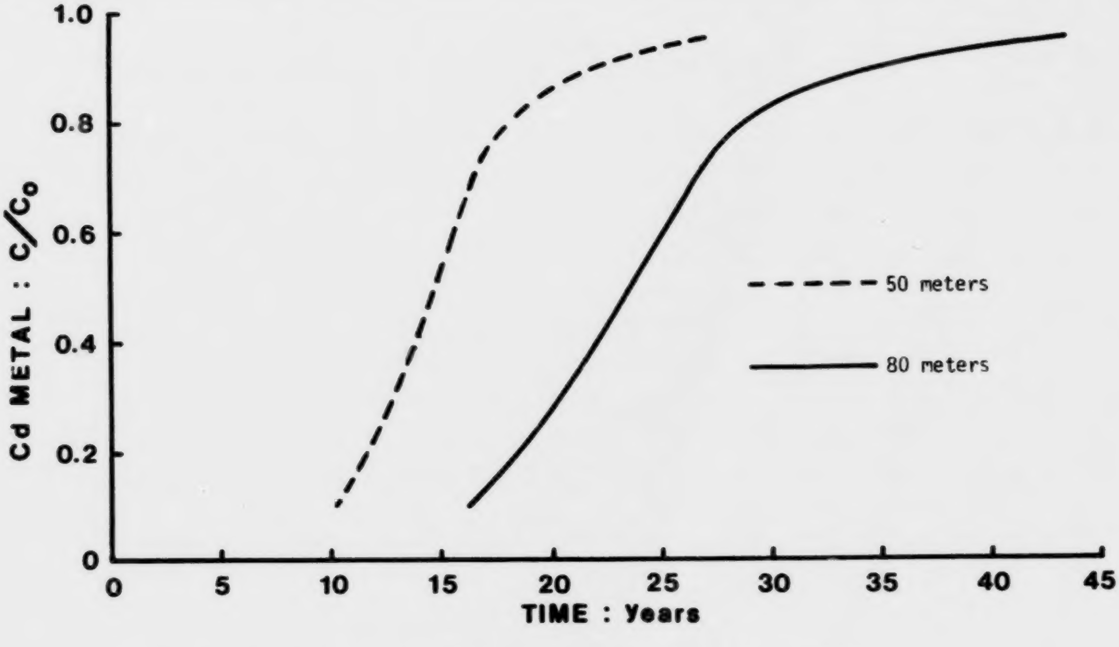


Figure 6. Breakthrough curves at 50 and 80 meter depths for Cd.

It should be stressed that these equations need further refinements and field testing before unqualified reliability can be placed on their use by landfill designers. We are in the process of such refinements now.

ACKNOWLEDGMENTS

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PREDICTING PERCOLATION THROUGH WASTE COVER BY WATER BALANCE

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ABSTRACT

A basic part of designing a new cover or evaluating the effectiveness of an existing cover on waste is a means of estimating the amount of water that percolates through. The water balance method appears to be suitable for approximate design despite some shortcomings in modeling the actual process.

INTRODUCTION

This paper summarizes a portion of a study on cover for solid and hazardous waste by the U. S. Army Engineer Waterways Experiment Station (WES). From 1977 to 1978, the study was concentrated on assembling and developing guidance on the design and construction of cover for solid waste. It was concluded from those efforts that a reliable tool for predicting percolation was needed for engineering soil cover design. This paper reviews the utility of one such predictive tool.

Background

The principal products of the WES study to date are four reports and papers.(1-4) The first report is an interim presentation of the subject which was distributed for external review. Every conceivable function of soil and alternative covers for solid waste was addressed, and recommendations for the selection of material and the design of cover were made. The interim report also provided quick response to EPA's desire for background as an aid to preparing guidelines. A separate, short paper(2) summarized the general approach of this first phase of the study.

The next effort of this study was toward completing and publishing a comprehensive report on design and construction of soil and alternative covers. The state-of-the-art in soil mechanics and soils construction was used to expand the interim report and a final report has now been published.(3)

In the future, as cover construction becomes more and more guided by engineering design, an analytical tool for predicting the amount of water percolating through a cover will be needed. The background and techniques for analysis of and design for percolation through cover were summarized at the Fifth Research Symposium.(4) As a part of further efforts to improve the capability for predicting percolation the present paper offers a critical review of the most convenient predictive method, i.e., by water balance.(5)

Water Balance Method

Water balancing(5) amounts to recording and analyzing the excesses and deficiencies of water in soil (Figure 1) and, thus, is fundamentally sound as a tool for predicting percolation through a soil cover. Water input as precipitation is fairly well known from records at numerous weather stations, but the other major factors, surface runoff, evapotranspiration, and soil water storage, are critical because of their greater degrees of uncertainty.

Figure 2 shows graphically the water balance in monthly increments for 2 ft of loamy soil cover at Cincinnati,

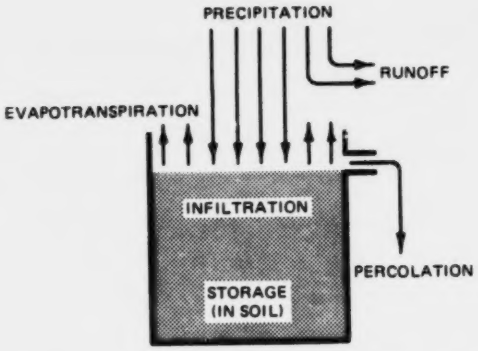

Figure 1. Schematic diagram of water balance in cover soil

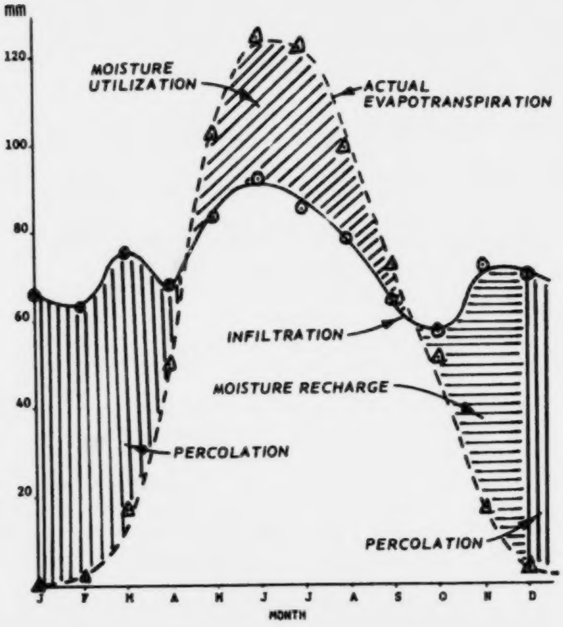

Figure 2. Water balance for Cincinnati, Ohio(5)

Ohio.(5) Also see Table 1. The monthly rainfall means are based on a 25-year record. The basic curve, for infiltration, was obtained by subtracting a reasonable runoff percentage from each monthly mean precipitation amount. The actual evapotranspiration curve is obtained by adjusting the potential evapotranspiration estimates (derived according to Thornthwaite & Mather(6)) for the availability of water in storage; thus in dry months soil water in storage decreases and may cause actual evapotranspiration to be less than potential levels.

APPRAISAL OF METHOD

The water balance method may be examined according to its sensitivity to variations in the major factors and according to its correspondence to the actual movement and distribution of water in soil in nature.

Conceptual Modeling

The water balance method is vulnerable to criticism in regard to failures in modeling the actual infiltration and percolation processes; e.g. the method makes no attempt to model changing infiltration capacity rate (Figure 3) which is known to vary as a function of time (for a constant source of water at the ground surface). Instead of functional relationships, the water balance method provides for an accounting in which increments of water are added and subtracted for the chosen time interval. Thus, the water that infiltrates over a period of a month, for example, is simply the difference between total precipitation falling in that one-month period and a given percentage of that precipitation considered to run off the surface. Similarly, the water subtracted as evapotranspiration is generalized to a total amount for the one-month time increment. The validity of the water balance method therefore depends on the validity of simple monthly additions and subtractions to represent very complicated processes that vary from day to day and within a collection of storm events.

In a similar manner the ultimate increment of water removed from the system as percolation is calculated as a remainder after an addition from precipitation and

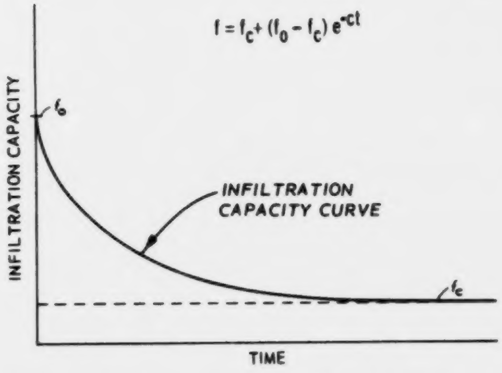

Figure 3. A general infiltration rate function

TABLE 1. WATER BALANCE DATA FOR CINCINNATI, OHIO(5)

Parameter *	J	F	M	A	M	J	J	A	S	O	N	D	Annual
PET	0	2	17	50	102	134	155	138	97	51	17	3	766
P	80	76	89	82	100	106	97	90	73	65	83	84	1025
$C_{R/O}$	0.17	0.17	0.17	0.17	0.17	0.13	0.13	0.13	0.13	0.13	0.13	0.17	
R/O	14	13	15	14	17	14	13	12	9	8	11	14	154
I	66	63	75	68	83	92	84	78	64	57	72	70	872
I-PET	+66	+61	+58	+18	-19	-42	-71	-60	-33	+6	+55	+67	+106
Σ NEG (I-PET)				(0)	-19	-61	-132	-192	-225				
ST	150	150	150	150	131	99	61	41	33	39	94	150	
Δ ST	0	0	0	0	-19	-32	-38	-20	-8	+6	+55	+56	
AET	0	2	17	50	102	124	122	98	72	51	17	3	658
PERC	+66	+61	+57	+18	0	0	0	0	0	0	0	+11	213

*The parameters are as follows: PET, potential evapotranspiration; P, precipitation; $C_{R/O}$ surface runoff coefficient; R/O, surface runoff; I, infiltration; ST, soil moisture storage; Δ ST, change in storage; AET, actual evapotranspiration; PERC, percolation. All values are in millimeters

subtractions for runoff and evapotranspiration. For realistic simulation of the actual process, it would be better to use a drainage function. In this way the important permeability characteristics of the soil could be involved. Otherwise, the soil permeability does not enter into the processes except in an indirect effect on the quantity of surface runoff, i.e. clayey soil does not transmit water as rapidly as sandy soil but instead promotes more surface runoff.

Sensitivity

A sensitivity analysis of the water balance method helps to pinpoint strengths and weaknesses for design purposes. A somewhat poorly known factor in water balancing is the evapotranspiration. The uncertainty inherent in using such calculated factors as input reduces somewhat the confidence that can be placed in the water balance method. Potential evapotranspiration calculated by different methods, however, seems to agree within a few tens of percent and the method cannot be condemned on this basis for approximate design work. Table 2 presents some values of potential evapotranspiration calculated directly from pan evaporation data for comparison to the values in Table 1 based on Thornthwaite and Mather. The correspondence is reasonably good.

The soil's capacity for storing water is the second major factor in the water balancing procedure that needs to be evaluated. Actual measurements of the capacity of various soils in the remolded condition and configuration of cover are scarce. At the present time this input into the water balance method is usually taken from some authoritative source in the existing literature. There can be considerable discrepancies among authorities in the actual values to be used, and in addition the root depth and condition of vegetation exert modifying influences. Consequently the available water storage space, i.e. between the field capacity and the wilting point, are indicated to vary by as much as a factor of three. In either case it has been shown(3) that the result as

TABLE 2. POTENTIAL EVAPOTRANSPIRATION BY TWO METHODS

Method	Potential Evapotranspiration, PET (mm)												
	J	F	M	A	M	J	J	A	S	O	N	D	Annual
Adjusted Pan Measurement*	-	-	-	75	102	105	119	91	61	45	-	-	-
Thornthwaite Estimation**	2	6	11	37	90	107	115	124	72	56	32	-	652

*For Versailles, Indiana in 1975
**For Cincinnati, Ohio in 1975

percolation predicted by the water balance method is not greatly affected by major changes in water storage capacity in the soil. Table 3 shows that increasing the storage capacity of a cover soil 3-fold may have only a modest effect on the predicted percolation.

One of the most critical decisions in water balancing concerns the handling of surface runoff. In this regard the choice of the appropriate runoff coefficient is most critical. Table 4 shows for the Cincinnati example(5) the effect of a range of runoff coefficients. It can be seen that the predicted percolation is quite sensitive to the choice of this coefficient, and the runoff coefficient may be the most important part of the whole design procedure. Incidentally, this conclusion focuses attention on the importance of designing the cover configuration for efficient and rapid runoff. Thus, the slope of the cover in general should be sufficient to promote rapid rill and sheet runoff and the main ditches, on somewhat gentler slopes, should be adequate for conveying the concentrated runoff beyond the edges of the landfill.

USEFULNESS OF METHOD

This study has confirmed the usefulness of the water balance method within certain constraints. It has been found that the method is simple but basically sound and, therefore, could be used for making design decisions. The range of variable conditions usually encountered when working with natural materials such as soil generally limits analytical design tools to providing conservative estimates of stability, adequacy, and so forth.

TABLE 3. PERCOLATION FOR RANGE OF STORAGE CAPACITIES

Water Storage Capacity, ST (mm)	Percolation, PERC (mm)												
	J	F	M	A	M	J	J	A	S	O	N	D	Annual
300	38	61	57	18	0	0	0	0	0	0	0	0	174
150	66	61	57	18	0	0	0	0	0	0	0	11	213
100	66	61	57	18	0	0	0	0	0	0	0	38	240
75	66	61	57	18	0	0	0	0	0	0	0	56	258

At Cincinnati, Ohio (see Table 1)

TABLE 4. PERCOLATION FOR RANGE OF RUNOFF COEFFICIENTS

Runoff Coefficient,* CRO	Percolation, PERC (mm)												
	J	F	M	A	M	J	J	A	S	O	N	D	Annual
0.51,0.39	0	8	27	0	0	0	0	0	0	0	0	0	35
0.34,0.26	20	48	42	4	0	0	0	0	0	0	0	0	114
0.17,0.13	66	61	57	18	0	0	0	0	0	0	0	11	213

At Cincinnati, Ohio
*Separate coefficients were used for wet and dry seasons

This review had indicated that expectable variabilities in evapotranspiration and soil water storage as used in water balancing have only modest effects on predicted percolation. On the other hand the runoff coefficient affects the predicted percolation in an important manner. Therefore the selection of the runoff coefficient should receive a great deal of attention. It might even be advisable to establish runoff-infiltration test plots to measure runoff and to compute runoff coefficients for available cover soils. Otherwise the designer is limited to using existing runoff coefficients or tables of coefficients from the literature where the variability is considerable.

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EFFECT OF ORGANIC CHEMICALS ON CLAY LINER PERMEABILITY

A Review of the Literature

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ABSTRACT

Permeability is the primary criteria for evaluating the suitability of clay soils for lining of waste impoundments. A review of available information has revealed the near-complete lack of knowledge about the possible impact typical waste impoundment contents have on the permeability of clay liners. The aims of this review have been to develop a list of organic chemicals found in waste impoundments; develop a list of clay minerals used to line impoundments, and review possible mechanisms for the failure of these liners.

INTRODUCTION

Proposed regulations for disposal of hazardous waste (USEPA, 1978) rely on the permeability of a clay soil liner as the primary criterion for judging the liners effectiveness at preventing the movement of toxic leachates into water below or adjacent to a waste impoundment. No single review is available that summarizes and interprets the available information on the possible influence of organic liquids on the permeability of clay liners. This report gathers and summarizes available information to allow better identification of cases where organic liquids may alter the permeability of clay liners. The basic approach has been to identify failure mechanisms and the organic liquids most likely to cause the failure. The information has been collected from a wide range of disciplines including soil chemistry, soil mineralogy, soil physics, chemical engineering, environmental engineering, petroleum engineering and geology. Related subject matter found useful included research reports on deep well waste injection, secondary oil recovery, soil water repellency, and clay-organic chemistry. Possible failure mechanisms discussed are catagorized as (1) Dissolution (2) Volume changes (3) Soil piping and (4) Miscellaneous.

ORGANIC CHEMICALS CONSIDERED

Essentially all available literature on the behavior of organic chemicals in soils relates to systems where water is the dominating fluid (Goring et al., 1972). Water is viewed as the carrier fluid and the organic chemical is in trace quantities. In the case of clay liners in direct contact with concentrated organic fluids, the various equations for organic adsorption by clay minerals have limited usefulness. A study is now underway to attempt correlation of various chemical properties with possible failure mechanisms. Table 1 is a list of selected organic fluids and the properties most likely to relate to their behavior in clay liners. Organic fluids placed in waste impoundments cover the spectrum of chemical species; the list is an attempt to select the most prevalent and representative of these compound types. The groupings of the organic chemicals which will be considered are acids, bases, neutral-polar and neutral-nonpolar.

TABLE 1. SELECTED CHEMICALS AND THEIR PHYSICAL PROPERTIES

ORGANIC CHEMICAL Forms	Example	BP(°C)	MP(°C)	Sp. Gr.	Mol. Wt.	Dielectric Constant			Water Sol. gm/l	Vapor Pressure at 20°C mm/Hg
						20°C	25°C	60°C		
Acids										
Aliphatic acid	Acetic acid	118	17	1.049	60.05	ND	ND	ND	infinite	14.4
Phenol	Phenol	182	43	1.072	94.11	ND	ND	9.1	82	0.2
Base										
Aromatic Amine	Aniline	184	-6.2	1.021	93.13	6.89	ND	ND	34	0.3
Alkyl Amine	Dodecyloammonium	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hetero-cyclic Amine	Pyridine	115	-42	.981	79.0	ND	12.3	ND	ND	14.0
Neutral-Polar										
Alcohol	Methanol	65	-98	.792	32.02	ND	32.6	ND	ND	92.0
Aldehyde	Butyr Aldehyde	75	-99	.817	72.10	ND	13.4	ND	ND	71.0
Glycol	Ethylene Glycol	198	-13	1.108	62.07	ND	ND	ND	ND	0.05
Alkyl Halide	Chloroform	61	-63	1.491	119.38	ND	ND	ND	8	160.0
Ketone	Ethyl Methy Ketone	80	-68	.805	72.11	ND	ND	ND	353	77.5
Neutral-Non Polar										
Alkane	Heptane	98	-91	.683	100.21	ND	ND	ND	0.003	53.0
Aromatic	Benzene	80	5.5	.878	78.11	2.28	ND	ND	1.780	76.0
Alkyl benzene	Xylene	139	-47	.868	106.16	2.37	ND	ND	0.198	6.5

CLAYS USED FOR CLAY LINERS

Clay Minerals - Introduction

Identification of clay minerals and their interaction with organic compounds has been accomplished by the use of Xray-diffractometry, and Infra-red spectroscopy (Greenland, 1965; Little, 1966; Theng, 1974). The clay minerals most often used for the lining of waste impoundments are Kaolinite, Illite or Montmorillonite. Considerations of upmost importance are the changes on the interlayer spacing and the consequential volume changes exhibited by each of these clays when exposed to organic chemicals that are likely to appear in a waste impoundments leachate. Each clay mineral is briefly described here along with a characterization of its interlayer properties. Table 2 gives the relative size of the three clay minerals being studied and also gives typical values for several other properties of these clays.

TABLE 2. TYPICAL VALUES FOR PROPERTIES OF KAOLINITE, ILLITE AND MONTMORILLONITE

	UNIT PARTICLE THICKNESS			Charge Per formula Wt.	Surface Area M^2/gm	Pure Mineral Exchange Cap. meq/100g	
	Contracted (nm)	Hydrated* (nm)	Δ Volume			Cation	Anion
Kaolinite **Non-expansive** **1:1 Lattice**	200.0	202.0	1%	0	8	10	pH dependant
Illite **Non-expansive** **2:1 Lattice**	20.0	22.0	10%	1.0	80	15	pH dependant
Montmorillonite **Expansive** **2:1 Lattice**	2.0	6.0	200%	.5	800	100	pH dependant <5

* Four water layers adsorbed for each available basal surface.

Kaolinite -

Kaolinite interactions with organic chemicals have been the subject of several studies (Conley et al., 1971; Olejnik et al., 1970; Carr et al., 1971; German et al., 1969). Kaolinite particles have a small negative surface charge. Adjacent layers of this mineral are strongly held together by hydrogen bonding. For this reason, kaolinite exhibits little interlayer expansion and adsorption of organic chemicals is largely confined to external crystal surfaces. Edges of the crystals exhibit broken bonds which give rise to a small number of highly pH dependant positive or negative charges.

Illite -

Illite has been shown to interact with organic chemicals (Macintosh et al., 1971; Greenland et al., 1965; Grim et al., 1947). Interlayer fixation by potassium ions usually permits no expansion of the space between illitic interlayers. Macintosh et al., (1971) however pointed out that one organic cation could replace these fixed potassium ions. This case is probably rare and exists only because the organic cation (dodecyclammonium) closely approximates the size and charge of potassium. Adsorption of organic chemicals will thus occur largely on the external crystal surfaces of this clay. Illites surface area , cation exchange capacity (CEC), and shrink-swell are intermediate between that of kaolinite and montmorillonite. The charge density on illite is the highest for the clays considered but due to its neutralization with non-exchangeable potassium ions, its CEC does not reflect this.

Montmorillonite -

The interaction between organic chemicals and montmorillonitic clays has been extensively studied (Parfitt, et al. 1968; Bradley, 1945; Hoffmann, et al., 1961; Greenland, 1963; Greene-Kelley, 1945; Theng, et al., 1967). This mineral has the smallest unit particle diameter of the three clay minerals considered. It also readily adsorbs polar or positively charged organic species on its interlayer surfaces. For these reasons, montmorillonite exhibits the greatest CEC, surface area, and shrink-swell potential. Montmorillonite can adsorb over 200% of its solid phase weight and consequently has the capacity for large shrinkage if its interlayer water is displaced by other fluids that yield a lower interlayer spacing. Montmorillonite has an intermediate charge density, but since its cations are exchangeable, its exhibits the highest CEC.

PERMEABILITY OF CLAY LINERS TO ORGANIC CHEMICALS

Clay soil permeability (K) is a numerical value representing its ability to transmit fluid. From Darcy's Law for liquid flux through a porous media, it can be seen that a soil K value is independant of the volume of soil, the volume of fluid passing, and the hydraulic gradient moving the water:

$$J = \frac{Q}{A} = KH$$

where;

J = Flux of a fluid $\mathrm{cm^3/cm^2\text{-}sec}$

Q = Flow ($\mathrm{cm^3/sec}$)

K = Permeability coefficient ($\mathrm{cm/sec}$)

H = Hydraulic head cm and

A = Crossectional area of flow ($\mathrm{cm^2}$)

and since:

$$Q = \frac{V}{T}$$

where:

V = Volume of fluid ($\mathrm{cm^3}$) and

T = Time (sec)

then:

$$K = \frac{V}{ATH}$$

Any change in the value of K will represent a change in the permeability of the media. For convenience of comparing the flow of fluids other than water, it is desirable to separate out the properties of the fluid which influence its movement.

$$K = \frac{V}{ATH} \quad \frac{(\eta)}{g\gamma}$$

where:

η = Viscosity of the fluid (gram/cm-sec)

γ = density of the fluid ($\mathrm{g/cm^3}$)

g = gravitational constant ($\mathrm{cm^2/sec}$)

Viscosity normalizes a fluids resistance to flow due to its cohesiveness, while the fluids density value normalizes the effect of gravity on its flow.

As part of the current study, the influence of selected organic chemicals on the permeability of clay liners is being tested. Central to these tests has been the development of a constant pressure permeameter suitable for permeability measurements on compacted clay liners subjected to organic chemicals.

FAILURE MECHANISMS

Clay Dissolution

Dissolution of a clay liner is brought about by an infiltrating chemical that dissolves the exposed surfaces of a pore or channel. Either organic acids or organic bases may solubilize portions of the clays structure. Acids have been reported to solubilize aluminum, iron, alkali metals and alkaline earths while bases will dissolve silica (Grim, 1973). Since clay minerals contain both silica and aluminum in large quantities, they are susceptible to partial dissolution by either acids or bases.

Clay Dissolution by Acids -

Pask, et al., (1945) boiled several clays minerals in acid and found the percent solubilization of alumina was 3% from kaolinite, 11% from illite and greater than 33% from montmorillonite. Grim (1968) found the solubility of clays in acid "varies with the nature of the acid, the acid concentration, the acid-to-clay ratio, the temperature and the duration of treatment." He also found that the action of an acid on clay was enhanced when the acid had an anion about the same size and geometry as a clay component. This would permit even weak acids to dissolve clays under some conditions.

Hurst (1970) found that the permeability of geologic formations could be increased by pumping in acetic or formic acid. Johansen, et al., (1951) reported flow increases for water wells following their treatment with a solution containing citric acid. Grubbs, et al., (1972) cited acid waste as the probable causal agent in the permeability increase of carbonate-containing minerals. Xray diffraction studies of the four clay minerals injected with acid waste showed them to be dissolved or completely altered. Diffraction peaks showed the most variability with montmorillonite clays.

Acidization is the name used for the process of permeability increase by acid mineral dissolution. This process is widely used to increase the permeability and hence the productivity of oil wells (Sinex, 1970).

An everpresent source of organic acids in waste impoundments are anerobic decomposition by-products. These include acetic, propionic, butyric, isobutyric and lactic acid. Anerobic decomposition will yield the carboxylic acid derivatives of whatever organic fluids are placed in the impoundment.

Material that incrusts at the base of wells used to inject waste usually consist of calcium, magnesium and iron carbonates, along with imbedded sand and clay particles. In order to remove the carbonate compounds, they must be dissolved and then held in solution against precipitation forces. Dissolution is usually accomplished with a strong acid. At this point, calcium will reprecipitate (as calcium sulfate in the presence of sulfuric acid) unless it is chelated and remove by a flowing fluid. Chelating agents effective at preventing reprecipitation of various carbonates are Citric acid, Tartaric acid, and Glycolic acid (Anonymous, 1977).

Clay Dissolution by Base -

Bases also have been implicated in the dissolution of clay liners. Haxo, Jr., (1976) found in preliminary tests that Bentonite liners allowed the passage of both strong acids and strong bases in a short period of time. Nutting (1943) showed even extremely dilute solutions of alkali to be effective at removing silica from smectites by dissolution from the crystal lattice. As part of this study, the effects of three organic bases on clay liners are being investigated.

Volume Changes -

Volume changes in clay liners occur when there is a change in the water content of the clay. Adsorption of water on external surfaces occurs with all three clay minerals. For a given change in water content, the magnitude of volume change is dependant on the clay mineral type, the arrangement of the clay particles, the size of the clay particles, the surface area per unit weight of the clay, and on the kind and proportion of cations adsorbed to the clay. From Table 2, it can be seen that montmorillonite (and to a lesser degree illite) may cause problems associated with changes in the volume of clay liners. Two contracted lattice sheets of montmorillonite have a 2 nm thickness. The adsorption of water on montmorillonites interlayer surfaces gives this type of clay soil the potential for greater than 200% difference in volume between the dehydrated and hydrated state. On the other hand, Gieseking (1939) reported that montmorillonite lost its ability to swell when exposed to organic cations.

Extraction of Interlayer Water -

Extraction of interlayer water causes the shrinking and associated cracking exhibited by montmorillonitic soils (Baver, 1972; Grim, 1968). Cracking is a result of the clay undergoing three dimensional shrinkage. Where the rate of water extraction is not uniform, cracks will form in wet soil (Young, et al., 1975). The water content of a clay liner will change if an organic leachate displaces the water from the clay liner. To more fully understand how much water will be displaced by a given organic fluid, it is necessary to first understand the nature and forms water takes in a clay liner.

Consider a case in which the clay particles are initially surrounded by multiple layers of water. The thickness of the water between adjacent montmorillonite lattice sheets would effect the plasticity, interparticle bonding, compaction and water movement within a clay liner. These properties change as the thickness of the interlayer water changes (Young, et al., 1975). Examination of the forces holding water to the interlayer surfaces in montmorillonite will assist in predicting the effects of an intruding organic leachate on the interlayer spacing.

It is widely believed that water layers immediately adjacent to montmorillonite interlayer surfaces are non-liquid, hexagonally structured, and held much more strongly than water layers further out from the surface (Grim, 1968). The thickness of this structured water varies depending on the adsorbed cation. Montmorillonite has a structured water thickness of 1 nm or four water layers per clay surface where calcium is the adsorbed cation. Sodium montmorillonite has a structured water thickness of .75 nm or 3 water layers on its surfaces (Grim, et al., 1945). Structured water should then yield an interlayer spacing of 1.5 nm and 2.0 nm for sodium and calcium montmorillonite respectively. Glaeser (1949) found a similar relationship to hold for montmorillonite where acetone was the interlayer fluid. Glaeser found the interlayer spacings to be 1.25 nm and 1.51 nm for a sodium and calcium montmorillonite respectively after the clay was dehydrated and subsequently exposed to acetone.

These surface-bound layers of water are held strongly to the clay. They represent however only a part of the interlayer water. The water layers further out from the clay surfaces are held in place by hydrogen bonds. The hydrogen bonded water extends back to the structured water layers anchored to the clay surface. These outer layers of water would easily be displaced by an intruding fluid. If the fluid lacked water's large dipole moment or its ability to hydrogen bond, a decrease in interlayer spacing would probably result, since fewer layers of organic molecules would be retained. If the intruding fluid had a higher affinity for the clay surface than the structured surface layers of water, large decreases in interlayer spacing should be possible, since some of the more tightly bond water would be removed.

Clay Wettability -

When a fluid adsorbs to a surface, that surface is said to be wetted by the fluid. Clay surfaces in a clay liner are initially wetted with water. If a permeating organic fluid has a higher affinity for the clay surface, the clay may become organic-wet. Petroleum engineers commonly refer to surfaces with oil adsorbed as being oil-wet (Raza, et al., 1968). Water and oil are said to compete with each other for solid surfaces in oil reservoirs. A quantitative measure of the preferential wettability of a clay surface for water and an organic fluid can be represented as the difference between the water-clay and organic-clay interfacial energies as represented by the Young-Dupre equation (Admas, 1941).

$$(\gamma\ org:c) - (\gamma\ w:c) = (\gamma org:w)(\cos\theta)$$

where:

$\gamma\ org:c$ = interfacial energy between the organic and clay (dynes/cm)

$\gamma\ w:c$ = interfacial energy between the water and clay (dynes/cm)

$\gamma org:w$ = interfacial energy between the organic and water (dynes/cm)

θ = angle at the organic:clay water interface measured through water (degrees)

There is no direct method for measuring either the organic:clay or the water:clay interfacial energy (Raza, 1968). Their difference, however, is equivalent to the product of the water:organic interfacial energy and the cosine of the water:clay:organic contact angle (θ).(Figure 1).

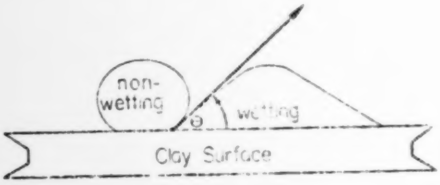

Figure 1. The contact angle(θ) measured through the wetting fluid is less than 90°. If the contact angle were measured through the non-wetting fluid, it would be greater than 90°.

Displacement of Interlayer Water -

If an intruding organic leachate displaces the anchored water layers, there will be no forces holding the balance of the interlayer water against gravitational drainage forces. In this case montmorillonite interlayer spacing (d(001)) would decrease from >>2 nm to whatever the interlayer spacing value would be for the newly adsorbed organic fluid. Table 3 is a list of the interlayer spacings for montmorillonite after exposure to organic fluids. There is an abundance of xray diffraction data for clay minerals with correlations to the interlayer cation, dehydration temperature and the immersion fluids pH, dielectric constant and concentration (Grim, 1968; Theng 1974; Barshad, 1952). The usefulness of this data is limited, however, because as a matter of standard procedure, the clay minerals are initially dehydrated. In order to more closely simulate the situation in a clay liner, there needs to be a series of xray diffraction studies on hydrated clay minerals. First, xray diffraction data is needed for the clay liner saturated with water as it would be prior to the impoundment of a waste. Secondly, xray diffraction data is needed for the same clay liner after organic leachates have permeated the clay. If a substantial interlayer spacing decrease is observed for the second set of xray diffraction data, shrinkage cracks may be anticipated for that particular liner-waste combination.

In a waste impoundment, the affinity an organic leachate has for the hydrated clay surfaces will determine if it will displace the water. Since the clay surface is negatively changes, organic leachate components that are positively charged or uncharged but polar will have an affinity for clay surfaces. Since the water on the clay's surface is several layers thick, water solubility will also improve an encrouching fluids access to the clay surface. The strength with which water is held to clay surfaces will vary with the cations adsorbed to the clay and the clay's charge density. These factors may change from one place to another in a clay liner. In order to predict interlayer spacing and permeability of inplace clay liners, a series of xray diffraction studies should be undertaken on the range of liner-waste combinations likely at a given site. After a leachate is in place in a liner, the charge density of the clay will effect the resulting interlayer spacing. Weiss(1963) found the interlayer spacing after exposure to alkylammonium ions to be 1.3 nm, 1.9 nm and 2.76 nm for montmorillonites with low, medium, and high charge density respectively.

It should be understood that

TABLE 3. INTERLAYER SPACINGS OF MONTMORILLONITE-ORGANIC COMPLEXES

Compound	Interlayer Spacing Ca. Sat.	 Na Sat. nm	Dielectric Constant 20°C	DiPole Moment*	Dehydrated temp. °C
Benzene	1.0	.99	2.3	0	250
Benzene	1.52	.99	2.3	0	150
Methanol	1.71	ND	32.35	1.66	250
Ethanol	1.70	1.34	25.00	1.70	170
Ethanol	1.70	1.35	25.00	1.70	250
N-Butanol	1.52	1.32	17.70	1.66	20
N-Butanol	1.45	1.32	17.70	1.66	170
N-Butanol	1.45	1.32	17.70	1.66	250
N-Decanol	3.68	ND	5.0	1.7	250
Paraffin	1.45	ND	2.10	0	20
Paraffin	.99	ND	2.10	0	250
H_2O	1.92	1.87	78.5	ND	250
Methy Ethyl Ketone	1.73	ND	18.85	2.74	250
2.1M β Alanine	2.05	ND	150.0	ND	250

* (x 10^{-18} Electro Static Units)

From Barshad (1952).

organic leachates may cause either shrinking or swelling of clay liners. Barrier (1978) reported swelling of montmorillonite clays as a result of exposure to several forms of acetonitrite, xylene, cyclopentane, alcohols,glycols and ketones. A liner which has swelled and heaved may loose its intergrity during heaving, or it may shrink later when water replaces inbibed organic chemicals.

Soil Piping -

Underseepage as the result of soil piping is an ever present danger in earthen dams. Mansur, et al., (1956) describes piping as "the active erosion... of soil from below the ground surface which occurs as a result of substratum pressure and the concentration of seepage in localized channels." Jones (1978) found the early stages of piping development to be associated with vertical contrasts of the structure and permeability in soils. Soil piping was also associated with shifts in a soils pore size distribution toward macropores with no corresponding change in total porosity. A reactive fluid may enlarge the surface area of a pore by dissolution of the pore wall and by the eventual dissolution of the soil matrix between two pores. While a fluid's reactivity is reduced by its action on the pore wall, the size increase in the pore will increase the rate of delivery of the fluid to the pore. In this manner, any difference in the pore size distribution of a clay liner may be magnified with time. Schechter et al., (1969 found that wormhole formation was the result of a reactive fluids preferential flow in larger pores. He went on to say that a quasi-equilibrium is reached where further growth in a pore is limited by the rate of difffusion of the reactive fluid.

Mitchell (1975) found that quick clays were often associated with the presence of organic compounds possessing strong dispersing characteristics. Quick clays act as viscous fluids and hence have no structural strength. Quick clays are susceptable to erosion caused be seepage. Seepage by reservior waters into dams have been reported to have caused dispersive piping and eventual tunneling all the way through earth dams. Tunneling was reported to occur in soils with a local permeability of 1×10^{-5} cm/sec.

Differential solution and subsequent leaching, especially with calcareous sediments, was reported to result in the formation of channels, sink holes, and cavities (Mitchell, 1975).

Cedergren (1967) reported that differential leaching of limestone, gypsum and other water soluble mineral components can lead to development of solution channels that get larger with time and substantially increase permeability.

He warned not to underestimate the importance of minor soil and geologic details on the permeability of soil formations as they cause the majority of failures in dams, reservoirs and other hydraulic structures.

Cedergren (1967) concluded that most failures caused by seepage can be placed in two catagories:

(1) those that are caused by soil particles migrating to an escape exit, causing piping and erosional failures;

(2) those caused by uncontrolled seepage patterns which leads to saturation, internal flooding, and excessive seepage.

Crouch (1978) found that so called tunnels, tunnel-gullies, or pseudokarsts will develop in dispersive soils where the soil-colloid bond strengths are low compared to the energy of water flowing through the soil. He found dispersive soils or those with low structural stability have been associated with tunnel erosion throughout the world.Other factors found to be related to tunnel erosion were ESP (Exchange sodium percentage), soil cracks, low permeability and hydraulic gradients.

In a study of the variables effecting piping, Landau, et al., (1977) noted a strong interaction between the chemical composition of the eroding water and compaction water content. Ion concentration seemed to have little effect on soil piping suseptibility for mixed illitic and kaolinitic clay loam compacted dry of optimum. For the same soil compacted wet of optimum, soil piping suseptibility was highly related to ion concentration in the eroding water. Landau (1977) postulated that the wet of optimum compaction produced a more parallel orientation of the soil particles which increased the effect of osmotic repulsion. Consequently the ion concentration of the soil water would have a relatively greater effect on dispersive forces in a soil compacted wet of optimum. When low ion concentration eroding water is combined with wet of optimum compaction, Laudau, et al., (1977) reported an exceptionally low resistence to internal erosion. These findings are felt to be especially important due to the long standing practice of compacting clay liners wet of optimum to produce the minimum initial permeability possible for a given compactive effort.

Piping involves the slaking of soil particles. Slaking is defined as the disintegration of unconfined soil samples when submerged in a fluid. Moriwaki, et al., (1977) investigated the dispersive slaking of sodium and calcium saturated kaolinite, illite, and montmorillonite. All the clays slaked by dispersion when saturated with sodium with the process proceeding faster with sodium-kaolinite and sodium-illite. Sodium-illite swelled slightly while sodium-montmorillonite's dispersion was preceded by extensive swelling. Sodium-kaolinite underwent no visible swelling while dispersing. For the calcium saturated clays, illite dispersed much more slowly while the rate of dispersion increased for kaolinite and montmorillonite. Calcium-kaolinite was thought to disperse faster because of its higher permeability relative to sodium-kaolinite. Sodium-montmorillonite was thought to disperse slowly because of the large degree of swelling it underwent would lower permeability, thus slowing water entry and retarding dispersion.

MISCELLANEOUS

Failure Mechanisms

There are a variety of situations that may increase the permeability of clay liners beside those three discussed in detail here. The phenomena causing the permeability increase may not be fully understood but they are presented here for their possible usefulness in future research.

Miller, et al., (1975) found the permeability of a soil to increase as water flushed out an earlier application of a surfactant.

Grubb, et al., (1973) found that methyl alcohol increased the permeability of a core previously injected with oil-base wastes. He also noted the use of solvents, organic acids, surfactants, alcohols, and emulsion breakers for permeability enhancement in deep well injection operations.

Letey, et al., (1962) observed an increase in the infiltration rate with time for water-repellent soils. He felt this was due to the progressive neutralization of the soils water-repellency as the depth of infiltration increased.

In a later study, Letey, et al., (1975) found that permeability increased with time if there is a substance in the soil that would dissolve into the water and decrease its surface tension.

Brant (1968) found an increase in the water permeability after a soil was treated with 4-t-butyl Catechol. He postulated that the increase was due to the soil matrix being rendered more stable to water flow yielding a decrease in the migration of soil particles.

Watson (1968) found surfactants acted to stabilize soils against dispersion and swelling, thereby preventing a decrease in permeability values at certain surfactant concentrations.

Wolstenholme (1977) stated that solvents of low viscosity are "by their very nature" leachable and able to extract organic components from otherwise dry waste. Lower viscosity would significantly increase the rate of a fluid's movement through a clay liner.

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ASSESSMENT OF LINER INSTALLATION PROCEDURES

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ABSTRACT

Southwest Research Institute is presently conducting a study to identify current methods and equipment used to (1) prepare supporting subgrade and (2) place liners at various impoundments in the United States. Subgrade preparation and liner placement activities have been observed at fifteen sites to date. The sites selected have included landfills, wastewater impoundments, and potable water reservoirs. Information obtained during each site visit included:

(1) Methods and equipment used to prepare the subgrade upon which the liner is to be placed;

(2) Methods and equipment used to place the liner material;

(3) Special problems encountered and their solutions; and

(4) Important characteristics which must be considered during design and construction of an impoundment facility.

Various aspects of subgrade preparation and liner placement are discussed herein. Photographs depicting construction and placement activities are presented.

INTRODUCTION

The use of surface impoundments and landfills to store, treat and/or dispose of unwanted materials has been and continues to be common practice for industry and municipal agencies since these types of facilities have proven to be cost effective solutions to treatment and disposal problems. Recent studies have shown that the use of such facilities can result in subsurface migration of hazardous materials into groundwater resources.[1,2]

The Resource Conservation and Recovery Act of 1976 and proposed EPA regulations will require positive control of subsurface migration of contamination from many of these facilities where hazardous materials are stored.[3] Future treatment and/or disposal sites will likely have to be designed to prevent groundwater contamination. It is likely that impermeable liners with high integrity will find increased usage in the future.

The proper planning, design and construction of surface impoundments and/or landfills designed to contain hazardous wastes involve numerous steps, including the following: (1) defining facility function and geometry; (2) selection of a liner material which is compatible with the material to be stored or treated; (3) planning suitable subgrade preparation, proper liner installation, adequate seepage monitoring and collection provisions; and (4) developing appropriate post-installation operation and maintenance planning.

This study, which addresses subgrade preparation and liner placement, has the following project objectives:

(1) To identify current subgrade preparation procedures and equipment used to build surface impoundments and landfills;

(2) To identify methods and equipment utilized to install various liner materials; and

(3) To identify special problems which should be considered during the planning, construction, and operation of such facilities.

The following generic types of liners are intended to be included in this study: (1) compacted native soils (clays); (2) admixes (asphalt, concrete and soil cement); (3) polymeric membranes (rubber and plastic sheeting); (4) sprayed-on linings; (5) soil sealants; and (6) chemical absorbants. Construction sites where many of these materials are being incorporated into the facility design have been identified and visited. Field notes from interviews, along with photographs, are used to document observations at each visited facility.

In this paper, preliminary findings relating to subgrade preparation and liner installation are presented and discussed. It has not yet been possible to visit sites representative of each of the generic liner types listed earlier. Photographs illustrating many of the points discussed are included in the text.

APPROACH

First, a list of sites which could be visited by a field crew was developed. The development was accomplished by contacting liner material manufacturers, fabricators, installation contractors and national, state, and local governmental agencies. Manufacturers, fabricators, and installers are most aware of ongoing and/or planned jobs, particularly where bids have been requested. The authors were directed to specific installers who had more up-to-date scheduling information for their particular interests. Arrangements were made for site visits with the owner of the facility, and the agreement of the installer.

All pertinent information about each site is kept on a master scheduling list which is updated continually as project schedules change. Field visits are scheduled and conducted concurrently with ongoing site identification. Every effort is made to identify and select sites representative of the generic liner types included in the project plan.

To date, fifteen sites have been studied. The type of facility visited and liner installed are as follows:

Facility Type	Liner Type
Wastewater Storage	CPE
Evaporation	HCPE
Evaporation	CSPE
Evaporation	CSPE/PVC
Evaporation	Compacted Clay
Landfill	Soil Sealant
Potable Water Storage	CSPE
Evaporation	CPE
Landfill	CSPE/Clay
Spill Containment	PVC
Wastewater Treatment	EPDM
Landfill	PVC
Water Reservoir	Soil Sealant
Potable Water Reservoir	CSPE
Landfill	PVC

SUBGRADE PREPARATION

Introduction

Subgrade is defined as the support medium upon which a liner, either man-made or natural materials, is placed. The subgrade is critical to the ability of the liner to perform its intended function; i.e., minimizing fluid seepage. The following sections discuss two important aspects of subgrade preparation for a lined impoundment, compaction and soil sterilization.

Compaction

Adequate compaction of subgrade is critical to the integrity of any lined impoundment, as the subgrade serves as the liner support. Various pieces of standard construction equipment are used when a flexible liner is installed. Size requirements depend upon the magnitude of the job and the degree of compaction required. Figure 1 shows a small sheep's foot roller being pulled by a bulldozer. This is suitable for use up steep slopes where the total acreage to be compacted is small. Figure 2 shows a vibratory roller and compactor being used to smooth the floor of a water reservoir impoundment. This size and type of equipment is typical within the construction industry.

Most facility designs specify a subgrade compaction to a standard proctor density or modified proctor density. In the event that native soils require the addition of moisture to achieve the designated soil compaction densities, equipment must be used to supply water to the soil. Figure 3 shows the use of a watering trailer to apply water over a large area. These watering vehicles are commonly found around surface mining operations to control dust and are readily adapted for use in applying water to subgrade.

Many installers do not use rollers to finish and smooth the surface of the subgrade. Oftentimes, bulldozers or other earthmoving equipment are used as a compaction device, producing a rough surface texture. The surface must then be smoothed prior to placement of a flexible liner. Figure 4 shows a surface scraper being used to finish surface preparation prior to placement. This type of equipment removes much of the surface rubble and, depending upon the soil type, can provide very adequate subgrade for liner placement.

In the event that earthmoving equipment used for excavation leaves a rough subgrade, further work is required to prepare the subgrade for liner placement. Figure 5 shows the type of surface which can be left by earthmoving equipment. This surface texture is not considered desirable for placement of flexible liners and should be smoothed and further compacted. Oftentimes, the subgrade will require a large amount of rework prior to liner placement. This may be due to the addition of soils from off-site resulting in incompatibilities in soil textures. Figure 6 shows a disc used to mix two types of soils to produce uniformity prior to compaction. Discs are also used to mix soil sealants such as bentonite with the native soils prior to compaction and subsequent sealing.

In many parts of the country, a common problem with subgrades is the presence of rocks. Rocks may cause problems because of their size and/or because of jagged edges. Most installers believe that if a liner is placed over rocks, the probability of failure is increased. Figure 7 shows workmen making a final inspection to remove any rocks which might be present in a finished subgrade. These men are working ahead of the liner placement crew in an effort to insure that a very smooth subgrade is obtained.

Soil Sterilization for Vegetation Control

In many parts of the United States, there are certain grasses and other plants which are extremely tenacious and which can, in the growing process, puncture a liner. Figure 8 illustrates a 'salt grass' which is growing up through a flexible liner being installed in the western United States. This area had been treated previously with an herbicide; unfortunately, the herbicide used was not effective against grasses common to the arid regions of the western United States, but, rather, was designed for use against grasses more common to the humid eastern United States. The end result was that not all the seeds were killed, the grass grew up through the liner and, as shown in Figures 9 and 10, either individual patches were placed on each pin-prick created by the grass, or in the case where large areas of liner were affected similarly, areas of 300 to 500 ft sq were entirely replaced with new liner materials. It is imperative that the proper regional herbicide be used in a particular geographic area. Generally, it is best to apply the herbicide and then wait for a few days before placing the liner directly over the area which was treated.

Figure 11 shows a typical herbicide application at a liner installation. At this particular site, a problem with a 'brush grass' occurred after application of the herbicide. The liner was placed over the treated area immediately, without waiting for a few days to pass. The grass punctured the liner and repairs were required. The installer believes that by placing the liner immediately after application, the growth process of the plant was enhanced due to the warmth and moisture which collected beneath the liner.

PLACEMENT

Introduction

The following sections discuss various aspects of liner placement which usually require consideration during facility planning and construction. Comments are based upon field observations as well as discussions with installers and contractors. Discussions mainly involve flexible membrane liners due to the fact that the majority of sites identified and visited to date have installed this generic type.

Site Storage

Consideration must be given to proper storage of liner materials after they are delivered to the site. If a covered area cannot be provided, many manufacturers recommend that the liner material be covered with a light or reflective plastic to help prevent possible degradation due to sunlight and massive heat buildup. Figure 12 shows boxes of fabricated panels of flexible liner material being stored at a job site. Note that some of these have light colored plastic covers. The importance of this protection during storage at the site is a function of the type of liner being stored, anticipated weather, length of time the material will be stored on the site and ambient temperatures. If extremes of temperatures are anticipated, the liner should be stored under a protective shelter.

Securing Liners

Various problems arise in the field when attempting to secure liners either to the subgrade or to penetrations or other concrete structures which are found within the confines of a surface impoundment or landfill. Figures 13, 14 and 15 show a method of attaching liners in their anchor trenches, utilizing concrete. Figure 13 shows the liner coming up the side slope and extending through the slit trench. Concrete is then poured over the liner. Figure 14 shows the concrete as it has been poured to secure the liner. Figure 15 shows a finished portion of a fresh-water reservoir in which concrete was used in the anchor trenches.

Many anchoring trenches do not utilize the concrete method. Rather, fill material is placed over the liner which extends into the trenches. The trenches are generally of two varieties, the slit-type as shown previously and a blade-cut type which has a steep edge adjacent to the liner slope and a gently sloping edge away from the liner slope, almost like a truncated V. The final result of the blade type of installation is similar to the slit trench in that fill material is merely placed over the liner after it has been placed into the trench.

Figure 16 shows a concrete base to which liner must be attached. Of interest here, of course, is the differential raising of the concrete on one side of a crack which has developed in this concrete impoundment, necessitating lining by flexible material. Before this impoundment was lined, filter-fabric was placed in double layers over cracks such as these to ensure that the liner placed over the sharp edges of these cracks would not be damaged by future movement. When attempting to install liner on concrete, it is necessary to use batten strips of one form or another. Figure 17 illustrates a method of attaching a liner at the top of the concrete impoundment utilizing batten strips. Figures shown later show similar methods of attaching PVC batten strips to liner via expanding bolts.

Bentonite

Bentonite, a hydrous aluminum silicate, is a colloidal clay of the montmorillonite group. It swells in water. The use of a bentonite is common in areas where compatibility or soil tests show that the proper application will lower premeability to the desired level. The method of applying bentonite varies. One method which has been used is to place 100-lb bags on a grid pattern covering the entire subgrade. A large piece of equipment such as a disc is then driven over the entire area. The disc ruptures the bags of bentonite and hopefully spreads the material evenly. One problem with this approach is that if the disc is run only in one direction, the bentonite may not be spread evenly. Figure 18 shows the result of working the soil in only one direction. The location of each bentonite bag can be seen, and the uneven distribution of the bentonite is apparent as lighter areas trending up and down the side slope. If the 'disc in' method of soil sealant application is to be used, it is important that the equipment be pulled in both directions to assure even distribution of the soil sealant. Figure 19 shows a specially designed rake which has been successfully used to blend bentonite with soil. This rake is especially effective when the soil is sandy in nature and void of rocks or lumps of clay. The rake is dragged behind a tractor or bulldozer and will mix bentonite down to approximately 3 inches below grade.

A common method of application uses a standard soil spreader attached to the back of a dump truck. The truck, loaded with bentonite, is then driven over the impoundment surface. Bentonite can also be applied pneumatically when large areas require application. The bentonite is pneumatically forced through an applicator. This method requires the use of more expensive equipment and finds limited use.

Seaming

A common problem for field installation crews of flexible lining material is steep side slopes. When walking on steep side slopes the potential for injury of workmen due to falls is greatly increased. To allow field crew personnel to accomplish field seaming and anchoring, special accommodations must be developed. Figure 20 shows a simple 2 x 4 (wrapped with a filter fabric for cushioning) and ropes tied to it. This board is secured around the top of the berm, providing the field crew footing when placing the batten strip shown on the right, and when seaming the liner.

Poor quality seams result from the use of the wrong adhesive systems or the placement of liner and subsequent seaming occurring during adverse field conditions. Adverse field conditions include cold temperatures, excessive moisture and high winds. Figure 21 shows a field crew attempting to use a solvent adhesive in temperatures which are too cold for the specific type of adhesive system to work properly. The seams which resulted from the activity shown did not meet quality control inspection criteria and had to be redone. The use of heat guns in this particular case might have allowed the liner material to be pre-heated hot enough to allow the adhesive system to set. As a result of the time and dollar losses, a different adhesive system was later adopted and successfuly utilized at this particular installation.

It is very important that a proper adhesive system be used for a given climate or set of weather conditions at a job site. The installation contractor needs to be aware of potential problems with certain systems in regard to cold and excessive moisture and should have a backup adhesive system which can be used to provide adequate seams when the desired system is not working. When weather conditions get too bad (i.e., temperatures <50°F, rain falling, standing water, and/or winds in excess of 20 mph), seaming should be halted.

The geometry of a particular impoundment can cause an excessive amount of liner material to accumulate in corners. Figure 22 shows such accumulation. This material must be cut out in the corner and a suitable seam made. Figure 23 also shows the use of patching compounds on the concrete panels prior to placement of the flexible membrane liner. Most liner installers recommend placement of panels such that field seams run perpendicular to the toe of the slope or up and down side slopes. Some installers violate this general recommendation when installing materials which are reinforced and can be field seamed easily. The field seams reach complete strength rapidly and panels may be placed such that field seams parallel the toe of the containing embankment. Figure 24 illustrates the placement of panels where field seams parallel to the toe result. This type of placement may stress the field seam before a complete cure of the adhesive is realized. Inadequate adhesion due to the applied stress can cause 'fishmouth' to occur and eventually result in seam failure. It is best to avoid this type of field seaming.

Figure 25 shows a large wrinkle at a seam edge. This wrinkle is probably a result of improper spotting and stretching of the panel. These kinds of wrinkles demand additional corrective procedures, thus slowing field seaming activities. To avoid this type of problem, this panel should be laid as smooth as possible prior to commencement of seaming.

A flexible membrane liner panel placed in a field may weigh from 2,000-5,000 pounds. It is important when moving this panel that the field crew does not physically stretch the material, especially at the edge to be seamed. Figure 26 shows the use of plastic dowels which allow the crew members a means to grab onto the liner without stretching it. The liner will be rolled around the dowel and the dowel will serve as a handle. This simple technique to avoid stretching and to enhance the ability of the workmen to move the liner is very effective and used by many installers.

Field seaming often requires the use of heat guns or lighting which means that a power source must be available. Remote field installations may not have suitable power. Installers must therefore make provisions to supply their own power.

Figure 27 shows a small portable generator which can be moved onto the liner itself and can follow a field crew providing adequate electricity for seaming operations. Of course, multiple generators can be used as required.

Liner panels can be as long as 200-300 feet. With large, heavy panels it is difficult to maneuver the panel material adequately in order to minimize seams or wrinkles. Figure 28 shows a simple way to secure the liner as the field crew moves down the panel removing wrinkles. The two men shown standing on the liner are there to keep the liner from sliding over the subgrade while the crew removes the wrinkles by pulling the line taut without stretching the material.

Invariably, when seaming many thousands of feet of liner material, wrinkles will occur along the seams. This situation is shown in Figure 29. Careful seaming procedures will be needed to assure seam integrity when wrinkles such as these are present. Excessive wrinkles are an endemic problem when subgrades are rough or the geometry of the site causes unusually shaped or various size panels to be used. In Figure 30 one solution to the excessive wrinkles is to pull them into one flap, cut them out, lap seam and patch the entire area.

Depending upon the size of an installaation, one aspect of impoundment construction can be on-going while liner installation is proceeding. Figure 31 shows a large impoundment being filled with effluent while liner placement continues elsewhere. The entire area shown in this slide has been lined and soil cover applied. Liner installation crews are at work elsewhere on this site, but they are not shown on this photo. In many instances, the impoundment facility is placed into service prior to the final completion of liner placement.

During field seaming, it is important that a good foundation be provided upon which to work a field seam. A hard, flat surface (the best for rolling and seaming) is normally not present in most installations. Therefore, a portable board device can be used to provide a suitable surface upon which seaming can be done. Figure 32 shows such a board. A rope is attached to one end, the board is approximately 12" wide and 10' long and can be slid along beneath the field seam as the act of seaming progresses. Most field seams require some type of rolling or smoothing, especially if an adhesive is applied. A board such as this provides an excellent, homogeneous surface for such activities. The pad shown in Figure 33 serves as a kneeling pad for the field crew and is designed to reduce fatigue.

Oftentimes, the geometry of a site will result in the occurrence of excess material during the installation process. In Figure 34 the liner materials can be seen overlapping, resulting in an excess of material. This excess was inevitable in this particular job as the circular top perimeter was larger than the circular perimeter at the toe. In order to properly excise the excess material and still provide an adequate overlap seam, a vertical chalk line down the side slope was established (see Figure 35). The liner material was cut along this line and the excess removed to be discarded or used elsewhere.

Sealing Around Penetrations

Penetrations through liner materials require adequate sealing to prevent migration of fluid through the liner at the point of penetration. Oftentimes, boots are constructed which fit over a penetration and seal to the liner. Figure 36 shows a small boot that was placed around a grounding cable which penetrated through the liner. Such a boot, which was constructed in the field, can be sealed to the liner material using an adhesive system similar to that used for field seaming. Oftentimes for larger structures these types of boots may be fabricated in a factory and shipped to the site for installation.

Penetration of a liner by any designed means should be avoided if at all possible. If penetrations exist it is imperative that an excellent seal be achieved around any liner penetrations. Figure 37 shows an inlet pipe penetrating through the side slope of an impoundment. The black/dark liner shown around the pipe is being placed prior to the installation of a 'boot' which will surround the entire pipe. This 'boot' is shown in Figure 38. Note the use of a stainless steel strap mechanically sealing the boot around the perimeter of the pipe at the impoundment end. This boot, when sealed to the liner, will prevent the seepage of fluid into the subgrade adjacent to the pipe. It is advisable that the installer familiarize himself with the number and types of penetrations ahead of time in order to develop adequate plans to seal the liner around the penetrations to minimize leaks.

Figures 39, 40 and 41 illustrate a method for securing liner material to and around a concrete penetration in a soon-to-be lined impoundment. A small pad is shown in Figure 39. This pad is secured to the concrete base by the use of a recommended mastic. Liner is then slit and placed over the penetration and abutted against the concrete structure. More mastic is applied to ensure a good seal between the concrete and the lining material. On top of this, as shown in Figure 41, are placed steel batten strips through which anchoring bolts will be emplaced. Though this particular operation was viewed in the field, it is probably not as reliable as other methods of securing lining around penetrations. Leak paths have been left around the edges of the penetration and the concrete itself may be a pathway for materials to migrate out of the lined impoundment when it is complete.

Wind Damage

When installing membrane liners in the field, the installers must be aware of the potential damage caused by heavy winds. When winds exceed 20 miles/hour, the emplacement of membrane lining materials becomes extremely tedious and the probability of damage resulting from the wind's lifting of the liners, much as a sail is filled by the wind on the ocean, is enhanced. The use of weights to hold lining materials down is common within the industry. Generally, the weights are bags filled with sand or, in the case shown in Figure 42, actual rolls of liner material placed over the installed layers. Figure 43 shows rows of sand bags which have been laid adjacent to the edge to be seamed in the field. These sand bags serve two purposes: to hold the liner down in heavy winds and to hold the liner in place as the seaming process goes on. In some instances, it is impossible to stop liner materials from being lifted by the winds when the winds become too strong. Figure 44 shows a reservoir being lined. The reservoir has a concrete rim to which the liner material was attached. After the liner was attached to the concrete rim, the liner was left overnight during which a heavy wind arose, lifted the liner, tugged it and eventually ripped it away from the uppermost concrete edge to which it was sealed. Figures 45, 46 and 47 illustrate the damage caused by the wind when the sand bags emplaced on a liner in the field proved to be insufficiently heavy to hold the liner in place when a heavy wind arose overnight. Tearing of the liner material is evident, as is a stretching of the liner material. The damage shown in these slides required considerable retailoring of the liner material in the field at great expense of both time and money.

Occasionally, even when very large panels have been laid and seamed together, the wind will find a crevice beneath the panel and will enter that crevice, producing a bubbling-like effect which will then be wafted by the wind and may eventually, if allowed to continue, weaken the liner in place. Figure 48 shows the occurrence of such a wafting effect with a liner which is partially covered by soil materials. Two or three large bubbles of air are beneath it, and are migrating and moving rapidly. Continued movement of this type may weaken field-seams and actually tear the liner material.

Another means of anchoring liners is shown in Figure 49. At this site, landfill materials were used to anchor the liner once it was in place. Large piles of sand are shown, weighting down the underlying liner material.

There is probably no way to adequately insure that wind damage will not occur when winds in excess of 30 miles/hour blow in an area in which lining by membrane materials is progressing. The best way to avoid any wind damage is to first anchor materials as well as is feasible in the field arrangement. Any loose edges which are exposed in the direction from which the wind normally blows should be extremely well anchored. Do not leave exposed edges on the side slopes. The wind will have a good fetch across the bottom of an impoundment and will migrate up the side slope with a swirling motion, thus being able to pick up liner along an edge which is bared along the side slope. When planning field-lining activities for a given day, attempt to leave as few as possible of these bare edges which the wind can pick up.

In the event that any liner damage does occur due to wind action, repair is an immediate necessity. Tears will have to be repaired, stretched material will undoubtedly have to be replaced, and the efforts of the placement team will be confined for a period of time to redoing that portion of the liner which was damaged.

In the case of some jobs which are confined to concrete tanks and other structures, the swirling effect of the wind due to the Venturi-like shape of the containment area may present a serious problem to the eventual correct placement of liner materials. This problem can be lessened or avoided in some instances by using batten strips such as those shown in Figure 50. These strips are being placed over the liner material to hold it in place because of excessive swirling winds within the circular concrete structure which is being lined. This batten arrangement was devised in the field precisely to control the effects of the swirling wind prevalent at this particular installation.

Soil Cover on Liners

In the case of liners such as PVC, it is necessary to place a soil cover over the liner to protect the liner from the bad effects of ultraviolet radiation on the plasticizers and plastic materials within the liner. Interestingly enough, liners such as Hypalon, HPE and others have soil covers placed on them not because of their susceptibility to sunlight, but because the soil cover acts as a stabilizing agent, holding down the liner beneath. Figure 51 shows a wheeled vehicle which is pushing soil cover over a liner. Figure 52 shows a dump truck which is being driven over a liner to deliver soil cover.

There is a question as to whether the use of heavy equipment on liners will eventually cause the integrity of the liner beneath to be lessened. One installer uses the equipment shown in Figures 53 and 54 to transfer soil cover material to the top of the liner without ever placing his equipment on the liner itself. The controversy over the use of heavy equipment on liners continues, but there are some methods to alleviate potential liner damage from the over movement of heavy vehicles. For example, the contractor can vary the ingress/egress locations for the heavy equipment onto the liner, or he can limit the absolute weight of the equipment which is allowed to work on the liner. A third way is to use tracked vehicles or bulbous tires with relatively low weight ratios when working over the liner materials.

Figure 55 shows a liner which has become degraded and cracked and pulled away from the subgrade as a result of the soil cover being washed away from the liner and subsequent weakening from the ultraviolet radiation of the sun. This frame illustrates what the use of soil covers will avoid. It is interesting that this particular site originally had a soil cover, but the soil was washed away at this point by the activity of wind generated waves moving across the surface of the impoundment, lapping on the edge, carrying away the soil cover. In some instances, extreme measures such as rip-rapping or wave-deflectors may be required in order to ensure that the underlying liner is protected by a continually existing overlying soil cover.

Quality Assurance

One of the problems at a given site is the maintenance of high quality in the workmanship which is progressing at the site. Figure 56 shows a machine which is spreading water over the dusty roads over which heavy equipment moves near the site. This may seem a trivial matter, but the absence or lessening of dust is actually a very important condition to strive for at a site. If at all possible, dust should be kept nonexistent. The presence of dust will inhibit the sealing capabilities of various types of adhesive materials. When it is not possible to absent an area of dust, extreme care must be taken to clean seam edges before the actual seaming process occurs.

A problem which can occur in some types of materials, actually damaging the materials themselves, is an effect known as "blocking." In blocking, the materials which are packed for transport will seal to themselves in the presence of excessive heat or with age. The end result is that when the liner is unfurled for use in the field, portions of the liner will stick to itself, and may cause a release of adhesion with the underlying reinforcement material when it is present. Figure 57 shows a picture of such a 'blocking' condition on a piece of Hypalon ready to be installed in the field. This type of blocking will generally not occur singly, but rather will occur along a seam in which the conditions were ripe for its formation. Figure 58 shows the condition as it would appear when repaired in the field. The three patches in the upper center portion of the figure show the blocking condition which was repaired with an overlying sealing patch of Hypalon.

The integrity of seams is also an important factor to be observed in the field. Figure 59 shows a seam which contains many wrinkles; additionally, this seam illustrates what happens when solvent evaporates before actual adhesion occurs. The bubbles seen in the central portion of the figure represent points where solvent evaporated before the overlying liner material adhered to the underlying material. It is probable that the seam in this area has less integrity than in an area which is free of bubbles. If possible, this 'bubbling' condition should be avoided by sealing as soon after the application of adhesive as is advised by the manufacturer. If the 'bubbling' condition develops excessivly, the seam will either have to be redone or patched. The manufacturer's recommendations for sealing should also be reviewed in an effort to find a method to stop the undesired bubbles from developing. When edges are sealed, many times pathways for leakage develop at wrinkles even though the adhesive is well applied. When wrinkles which are potential leakage pathways develop, the wise contractor will ensure that there will be no leakage by placing a patch over the potentially offending area. Figure 60 shows such a patch as does Figure 61. Both these patches are of questionable quality and may need further evaluation and eventual replacement. Figure 62 shows the need for multiple patching which occurs when numerous wrinkles are present in a layer to be seamed to another layer which has numerous wrinkles. Each of the wrinkles represents a leak path which must then be sealed by the addition of the overlying patch. This particular figure shows three patches, one on top of the other. It is not recommended that this type of patching be done with wrinkles of this sort. Rather, all attempts should be made to smooth and remove the wrinkles; if this is not possible, it is best to consolidate the wrinkles into one large wrinkle which can then either be excised and sealed, or folded over, glued and sealed with one single patch on top.

Each site will generally have a Quality Control inspector. It is recommended that Quality Control inspectors operate in a pre-formulated plan, rather than a haphazard manner. This means that a well-defined plan for inspection should be developed prior to liner installation. Figure 63 shows the markings left by Quality Control inspectors as they went about inspecting the field seams and factory seams in one installation. This type of control should generate the best possible integrity.

SPECIAL DESIGN CONSIDERATIONS

Future Expansion

When a flexible membrane liner is included as part of the facility, the design should incorporate considerations on how the facility will be expanded in the future. Haxo et al have shown that aging of flexible membrane materials often results in changes in certain physical properties. This can be an important factor when considering adding on new liner material to existing liner material. Figure 64 shows a worker uncovering the edge of an existing liner panel which has been buried for several years. In this particular case, a new liner will be seamed or attached to the edge shown in Figure 64. Since this material has been buried for several years, it will be difficult at varying locations to get a good adhesion of the old and new liner materials. This situation resulted because proper planning for expansion had not occurred.

Figure 65 shows the incorporation of a method to plan for the expansion of a liner in the future. The figure shows a flap on top of the existing liner; this flap will seal the plastic strip shown in the figure to the existing liner. In the event of future expansion, the flap will be exposed, the polyethylene plastic removed and the new liner material seamed to the bottom of this flap. This assures a relatively virgin surface for seaming the new liner material to the old. Figure 66 depicts the flap which has been sealed into place.

Liner Selection Based on Use

The costs of liner materials often play a very important role in design. Different polymeric liners have different purchase and installation costs. For large impoundments, some design engineers are incorporating the use of two different liner materials to help decrease total facility costs. Figure 67 shows such a design. In this particular instance, the side slopes are a reinforced liner material, 36 mil thickness; the bottom of the impoundment is a 30 mil material, non-reinforced. The side slopes have been lined with reinforced material since the reinforcing fiber lends greater strength to the material and facilitates installation during hot weather. These two materials are both chlorinated polyethylene and, therefore, the seaming techniques at the toe did not require any unusual adhesive system or bonding technique. The cost savings in this design result from the use of a less expensive, thinner, non-reinforced material on the floor of the impoundment.

Figure 68 illustrates the use of a combination of two different generic liner materials seamed together at the toe of the impoundment. The material on the bottom is a PVC non-reinforced material; the material above is a reinforced Hypalon. This particular design was utilized to save money. These two materials are not directly compatible to field seaming and a marriage material was utilized to join them. Figure 68 shows a factory seam. The two materials shown in Figure 68 vary greatly in installed cost. The PVC is a much cheaper material than the Hypalon; the PVC was used on the floor of the impoundment because the total area there accounted for the majority of the square footage of the facility. The use of the reinforced Hypalon on the side slopes was decided upon because this material is resistant to sun induced aging. In addition, the reinforced Hypalon provides greater strength against the damaging effects of wave action.

Monitoring

Monitoring wells provide a means of determining if a liner is functioning adequately before any leakage from the liner can leave the immediate vicinity of an impoundment. Figure 69 shows a monitoring well casing located adjacent to an existing landfill. This monitoring well will serve as a source of groundwater samples which will be taken periodically to detect changes in groundwater quality. Monitoring wells are best situated hydraulically down stream from the landfill site. It is important that casings like this be protected against vehicle damage or vandalism while remaining accessible to sampling crews. Monitoring systems are an important part of facility design and will, undoubtedly, be incorporated more and more in the future.

Surface Covers

One method to prevent the production of leachate at an existing landfill is to install a flexible liner, much like an 'umbrella,' over the completed fill to prevent the inflow of rainwater or surface runoff. Figure 70 shows a completed landfill cover in the final stages of the application of the earth cover.

Gas Venting

One problem that can result from the use of a relatively impermeable liner is the containment of gases below the installed liner. If the liner is placed over material known to cause gas production, such as organics, the potential collection of gas is increased. When the potential for gas buildup is present, some provision must be made to relieve the ensuing gas pressure. Figure 71 shows an overall view of a facility where a liner is being placed for a landfill. Note the white PVC pipe stands projecting along the crest of the cover. These are gas vents and will serve to relieve pressure which might develop underneath the liner. Such gas venting is a very necessary control aspect at landfill installations.

Control of Surface Runoff

Another aspect in impoundment design is the prevention of surface runoff from encroaching upon the impoundment perimeter. This is important for two reasons: (1) such runoff may tend to violate the in tegrity of the berms or erode a soil cover which might be placed on the liner, and (2) one should minimize the amount of water contained in the impoundment and therefore increase the useful life of the facility. Figure 72 shows the use of a diversion dam located in the upper left hand corner. This dam will prevent surface runoff from flowing down into the impoundment.

Interestingly, some facilities with high evaporation rates actually channel runoff into their impoundments via surface routes in order to control the erosive effects. This is an important design consideration regardless of the magnitude of the facility.

Dual Liners

When added confidence is required, particularly for a facility where very hazardous materials will be stored, it is desirable to incorporate the use of dual liners. These may be a combination of soil, flexible liners, or specially treated soils. Figure 73 shows a facility incorporating two separate liners to prevent fluid movement into the subsoil. The upper layer is a soil cover over a flexible membrane liner; the third layer from the top is another compacted soil underlined with Fuller's earth. By incorporating two barriers against fluid loss, the owner of this facility increases the confidence that fluid will be contained.

Special Subgrades

A liner is often placed over a damaged or extremely irregular subgrade, which may be concrete, aggregated materials or even bedrock. In such instances, the design and installation must take into consideration the condition of the subgrade; any cracks that might be present, shifts in the surface elevation, or irregular, jagged edges must be ameliorated. Placement of a liner material over such differential settling or stress induced cracks or extremely irregular subgrades may cause eventual liner failure. Figure 74 depicts the placement of filter fabric over a 4-inch deep crack caused by differential settling beneath an existing concrete containment wall. The fabric material will protect the liner from tearing by preventing the liner from being "embossed" onto the concrete surface by the overlying weight associated with the fluid head in the impoundment. Note that on the right, fabric has been placed over the entire concrete surface, while on the bottom sand has been placed. The piece of fabric that the two workmen are placing will be an additional layer of filter fabric and will be covered again by a second layer. This particular location had an extreme crack, thus warranting the use of two layers of filter fabric.

Another site was visited where the irregular condition of the bedrock subgrade demanded that a cushioning layer of filter fabric be laid beneath the liner. Of course, the use of filter fabric adds additional cost of materials and installation time to a given job, but should increase the integrity of the given installation.

SUMMARY

As a result of project activities, lined surface impoundment and landfill construction sites have been visited in order to observe and assess subgrade preparation and liner placement procedures. During these visits, emphasis was placed on identifying construction and installation methods which provided acceptable solutions to the various problems encountered during the field activities. Photographs have been presented in this paper to show various aspects of facility construction and installation. Important items which should be considered during construction and installation were discussed. There exists in the liner industry literature, recommended acceptable procedures for installation. Often, the recommended procedures have to be modified to accommodate special problems or site characteristics. Accommodation which insures reliable construction and installation methods requires an experienced, knowledgeable installation crew to adapt to the various field situations. There are also unacceptable practices which must be avoided. This paper has attempted to present some of the problem areas, identifying both satisfactory and unsatisfactory solutions.

At the present, the final responsibility for any installation performing its intended function rests with the owner. Therefore, the owner must take an active part in the planning, installation and operation of a lined surface impoundment or landfill. It is the authors' opinion that a series of nationally accepted guidelines are needed, defining methods and procedures for the installation of various materials. Included in these guidelines should be a well-defined, meangingful, quality assurance program which can be employed by a prospective owner to insure field installation procedures will provide desirable results.

ACKNOWLEDGEMENTS

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3. U.S. Environmental Protection Agency. 1978. Hazardous Waste Guidelines and Regulations. Federal Register, Vol. 43, No. 243.

Figure 1. Sheeps Foot Roller used for subgrade compaction.

Figure 2. Vibratory roller used for subgrade compaction.

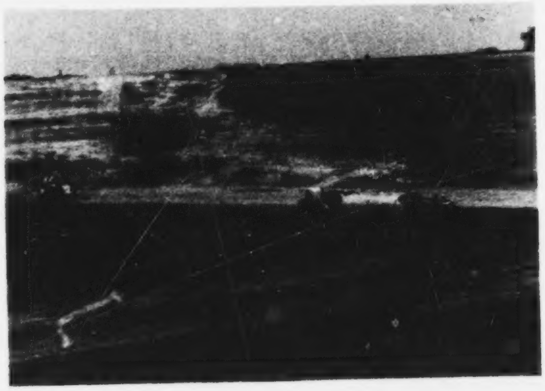

Figure 3. Large watering vehicle used for dust control.

Figure 4. Surface scraper used for final smoothing.

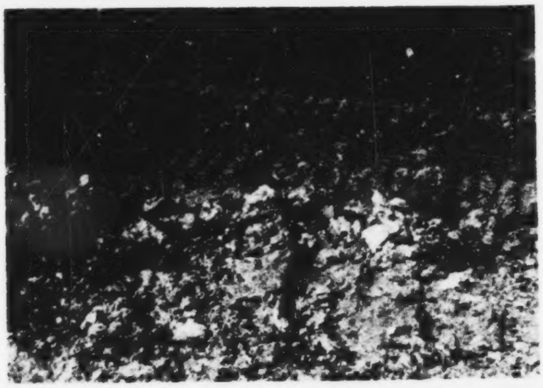

Figure 5. Undesirable subgrade surface texture.

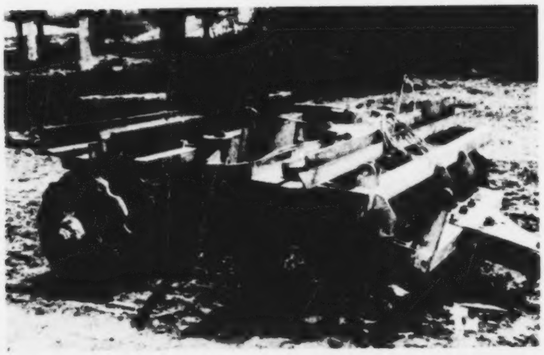

Figure 6. Disc suitable for soil blending.

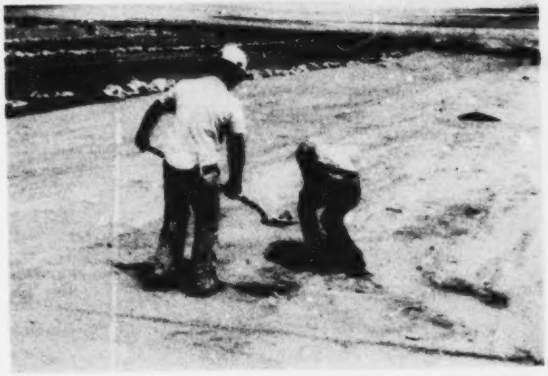

Figure 7. Workmen removing small rocks during subgrade inspection.

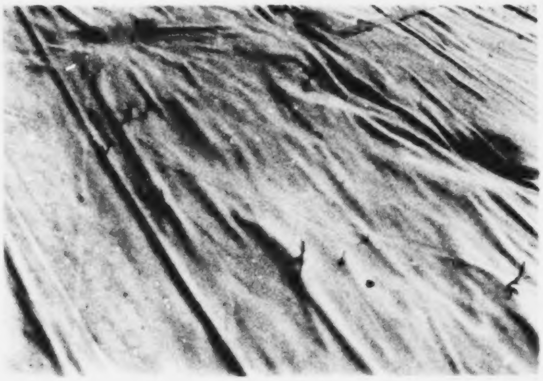

Figure 8. "Salt grass" growing through a flexible membrane liner.

Figure 9. Liner repair required due to "salt grass" damage.

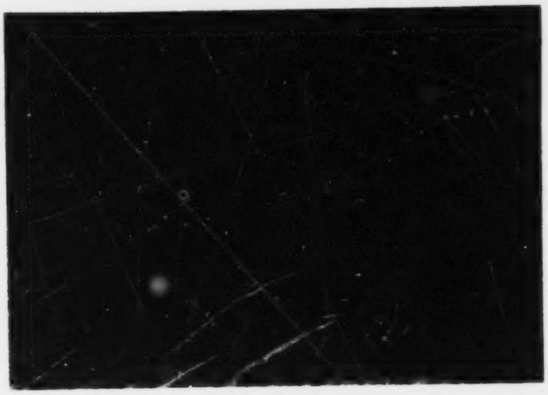

Figure 10. Liner replacement due to "salt grass" damage.

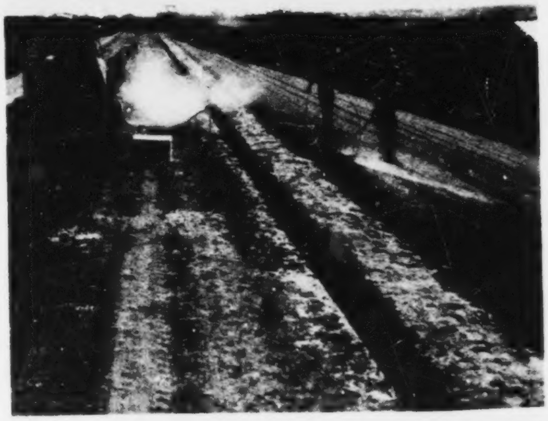

Figure 11. Application of an herbicide to the subgrade for soil sterilization.

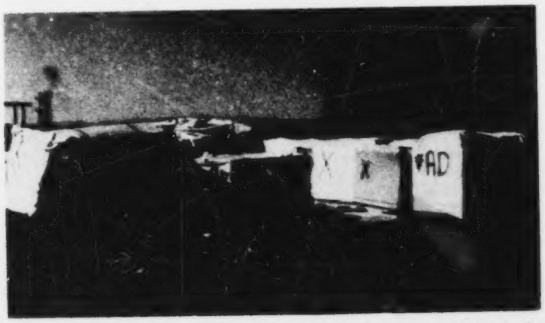

Figure 12. Site storage of liner material showing protective plastic covering.

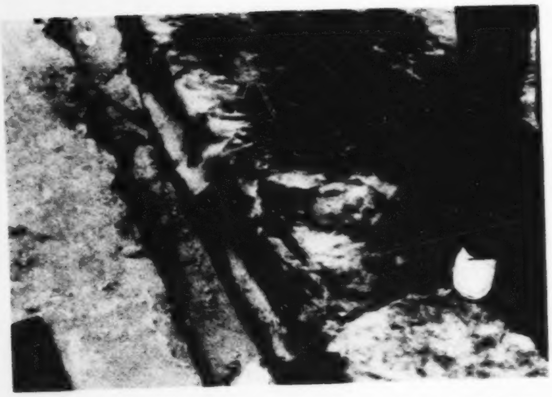

Figure 13. Initial placement of a liner into an anchor trench.

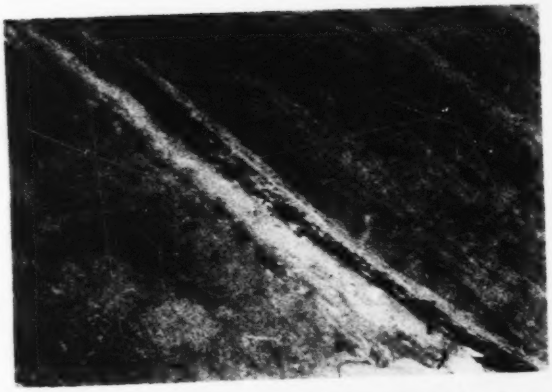

Figure 16. Differential settlement of a concrete subgrade.

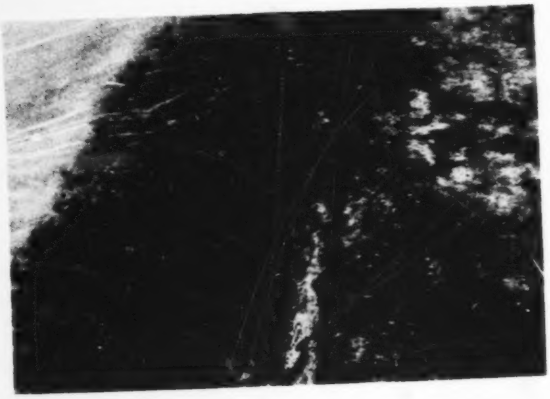

Figure 14. Anchor trench filled with concrete.

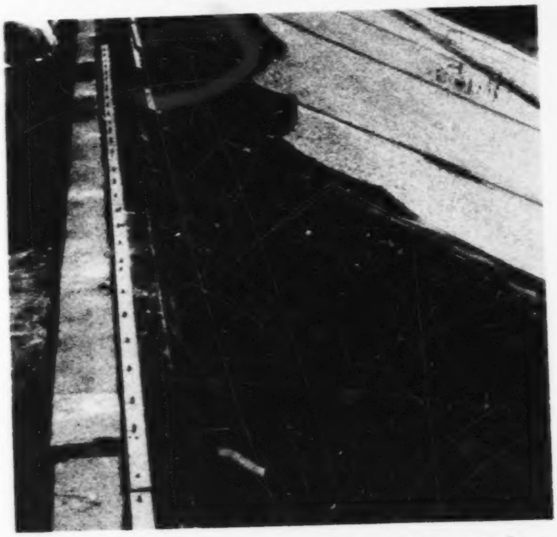

Figure 17. Stainless steel batten strips securing a liner to concrete.

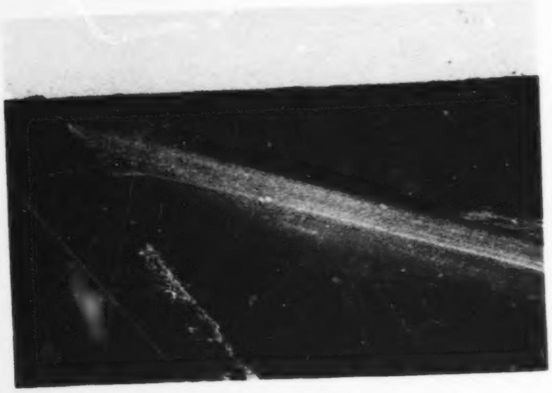

Figure 15. Finished anchor trench - concrete.

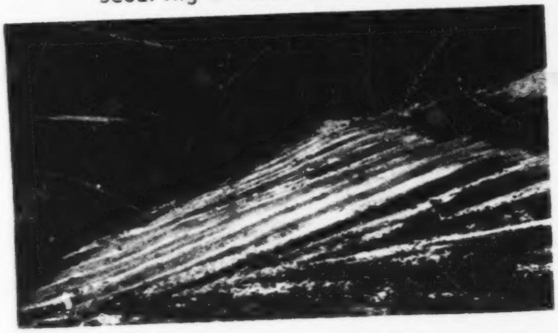

Figure 18. Bentonite applied to a soil where spreading was uneven.

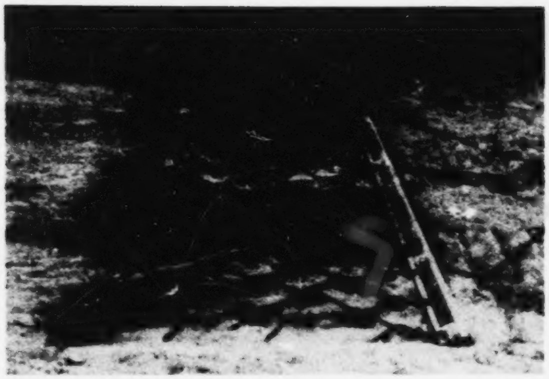

Figure 19. An iron "rake" used to blend bentonite and native soil.

Figure 20. Support board for working on steep incline.

Figure 21. Unsuccessful seaming with a solvent adhesive in cold temperatures.

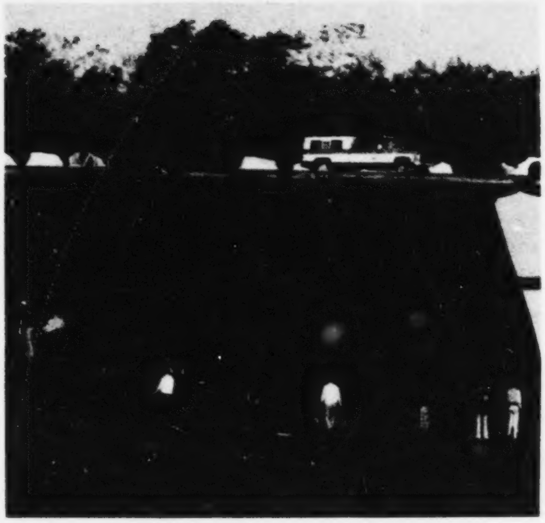

Figure 22. Excessive accumulation of liner material.

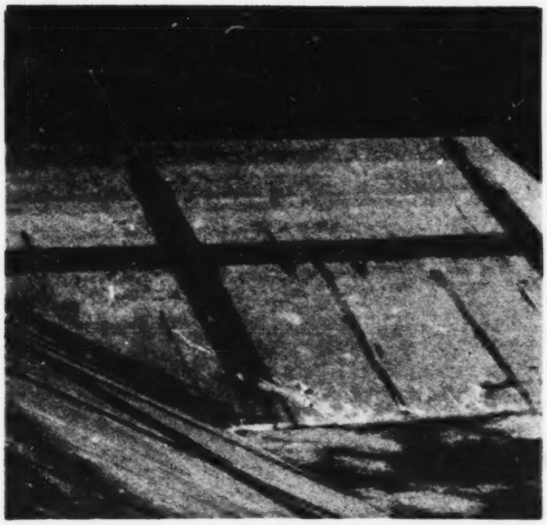

Figure 23. Patching compounds applied to concrete panel joints.

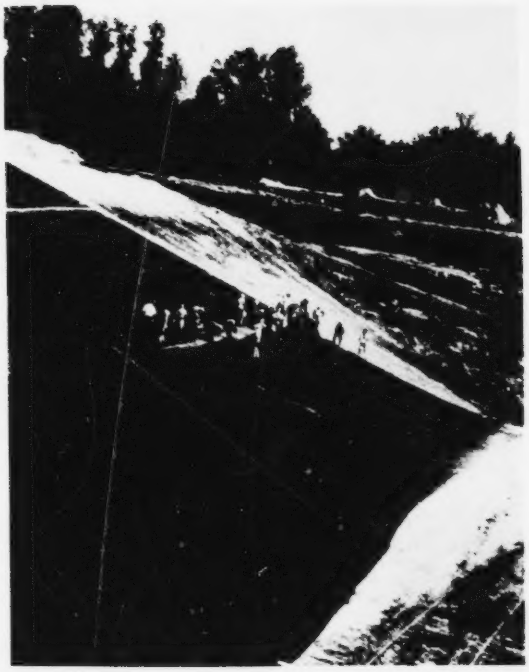

Figure 24. Field seams parallel to side slope toe.

Figure 26. Plastic dowels being used to pull liner panels.

Figure 25. Large wrinkle at edge of liner panel.

Figure 27. Field generator.

Figure 28. Removing wrinkles from panel.

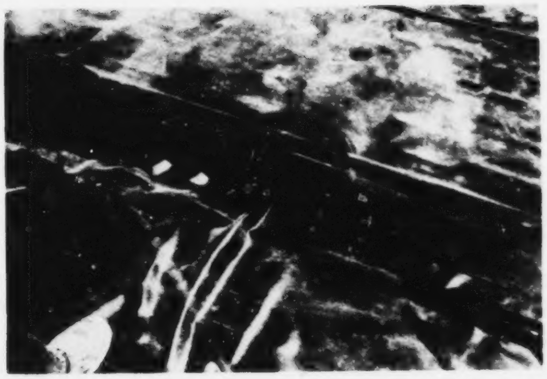

Figure 29. This seam wrinkle will require removal.

Figure 30. Repair of seam wrinkle.

Figure 31. An impoundment being utilized while liner placement continues.

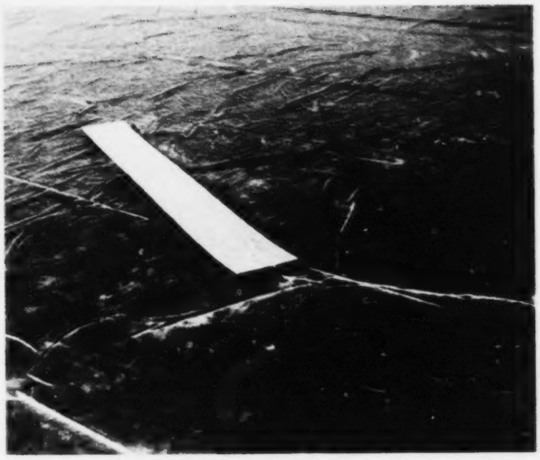

Figure 32. Seaming board.

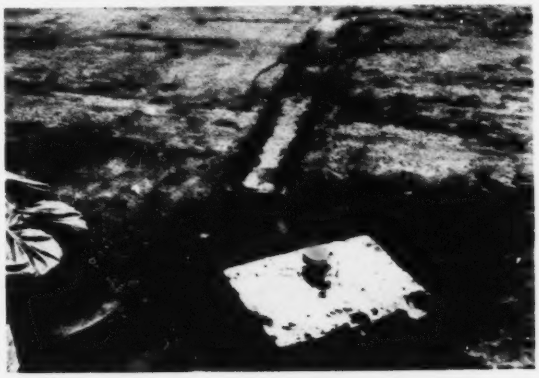

Figure 33. Knee pad used by field crews.

Figure 34. Material overlap.

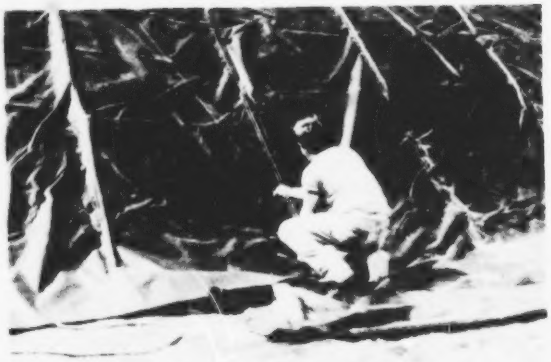

Figure 35. Use of a chalk line to mark a liner for removal of excess material.

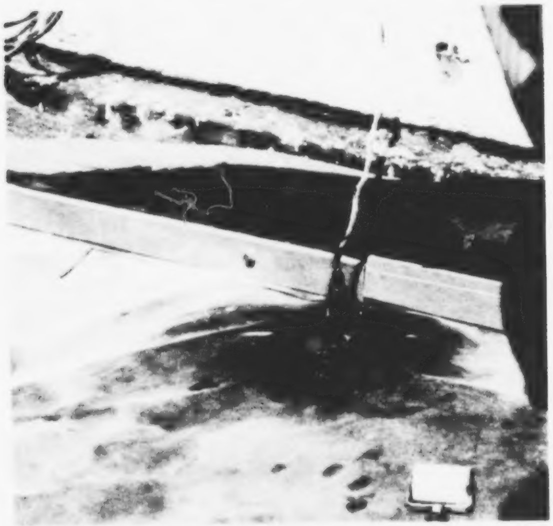

Figure 36. Field constructed boot for a liner penetration.

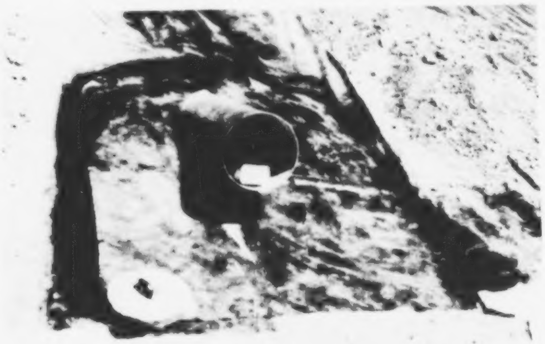

Figure 37. Pipe penetration being prepared for installation of a 'boot.'

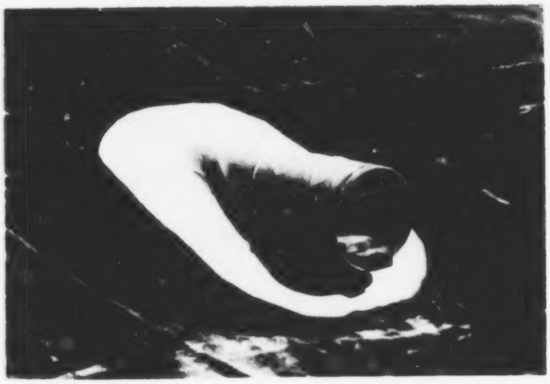

Figure 38. Completed boot installation.

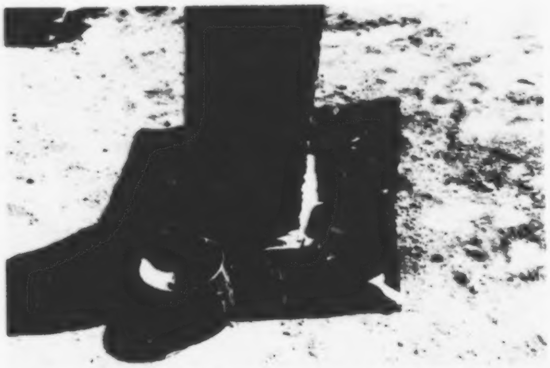

Figure 39. Liner pad around a concrete penetration.

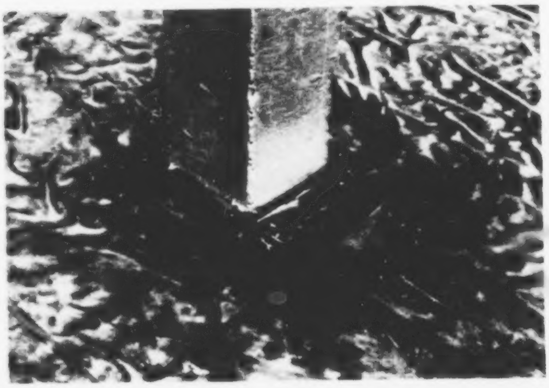

Figure 40. Pad prior to locating steel batten strips.

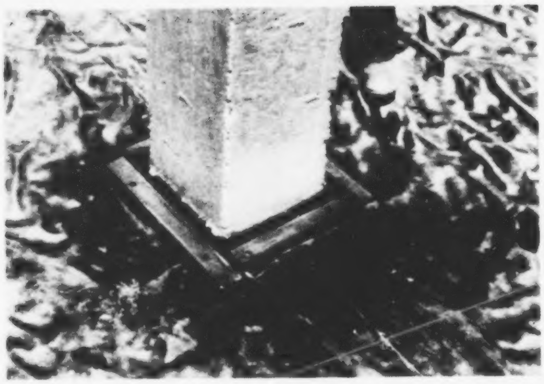

Figure 41. Placement of steel battens around concrete penetration.

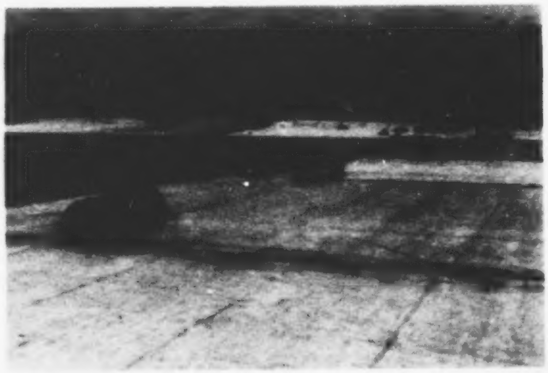

Figure 42. Liner panels used to prevent wind damage.

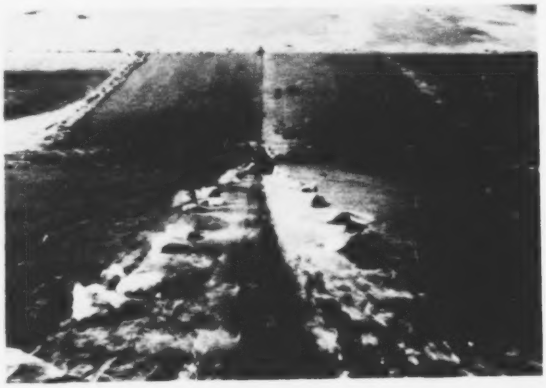

Figure 43. Use of sandbags along a seam.

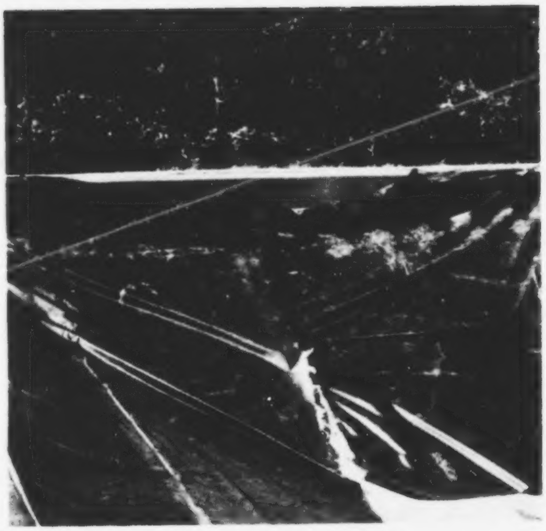

Figure 44. Wind damage.

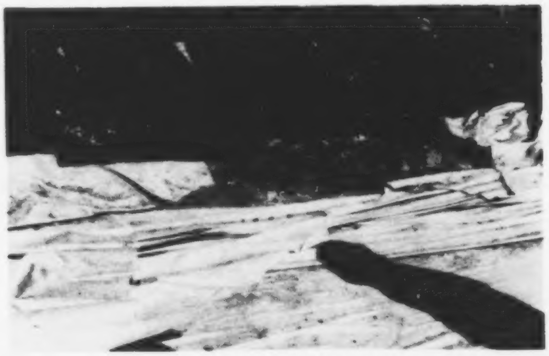

Figure 45. Wind damage.

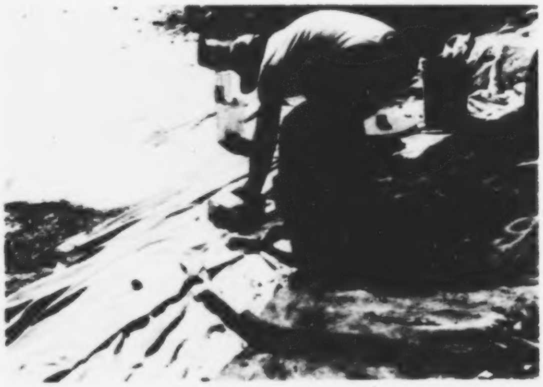

Figure 46. Wind damage.

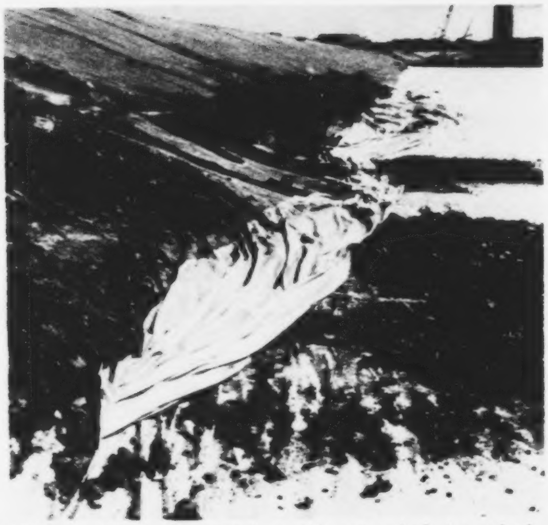

Figure 47. Stretching of material by wind.

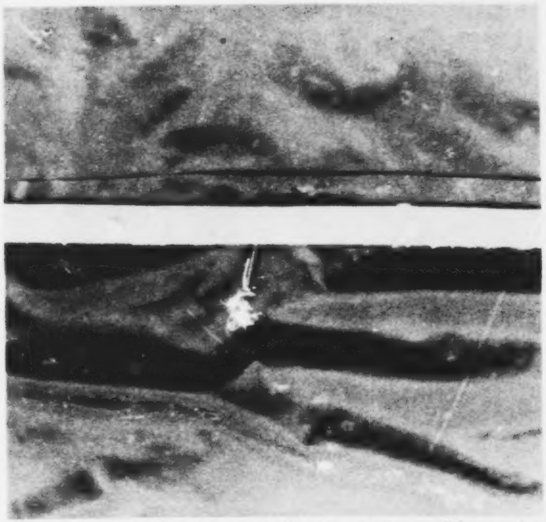

Figure 50. Batten strip to secure liner to concrete subgrade.

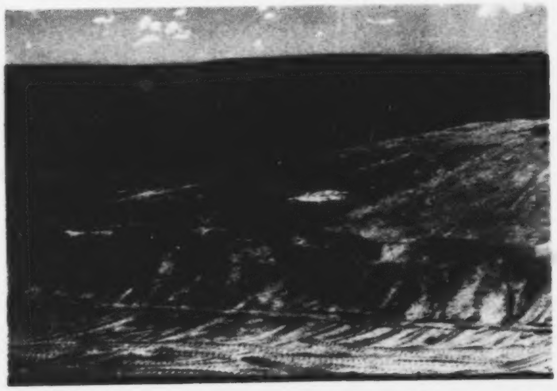

Figure 48. Wafting effect on a liner not secured by a soil cover.

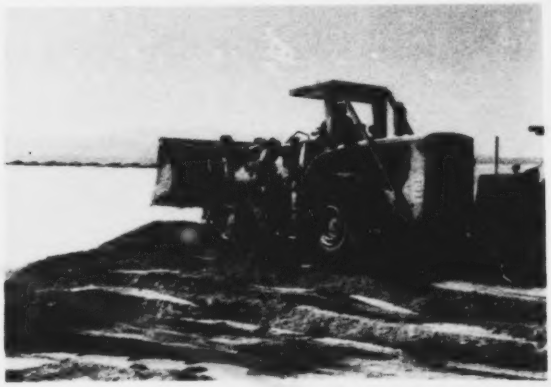

Figure 51. Rubber wheeled vehicle used for placing soil cover.

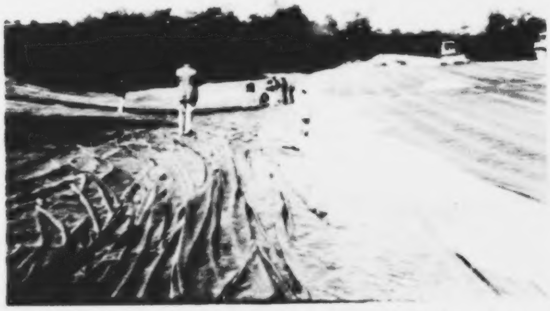

Figure 49. Use of cover material in place of sandbags.

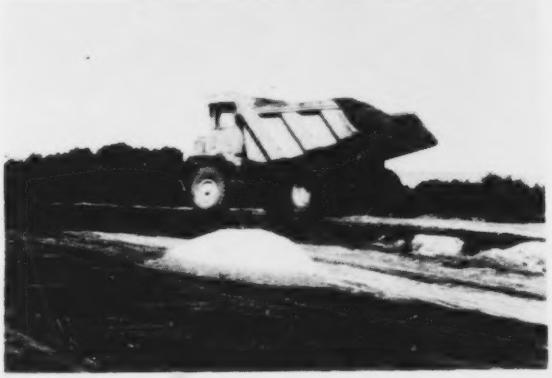

Figure 52. Large dump truck placing soil cover.

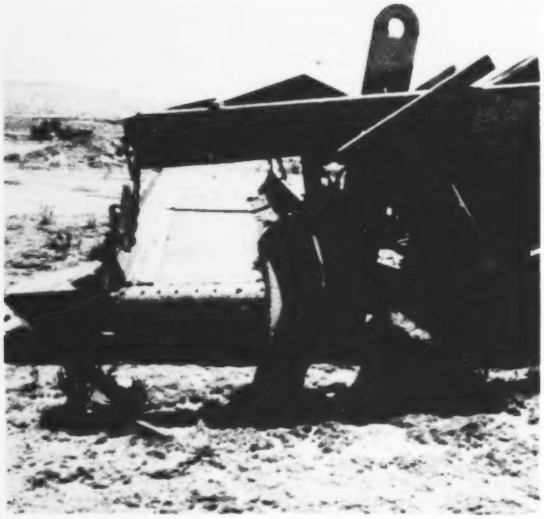

Figure 53. Equipment to place soil cover.

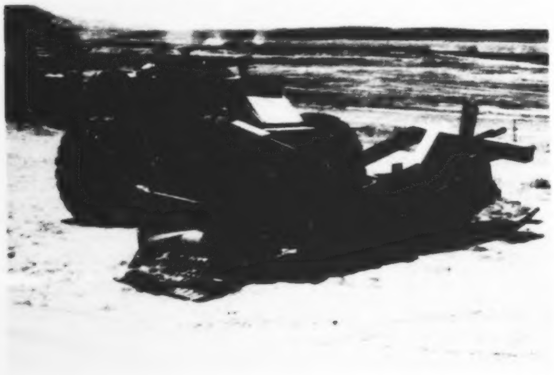

Figure 54. Equipment to place soil cover.

Figure 55. Results of sun aging and degradation.

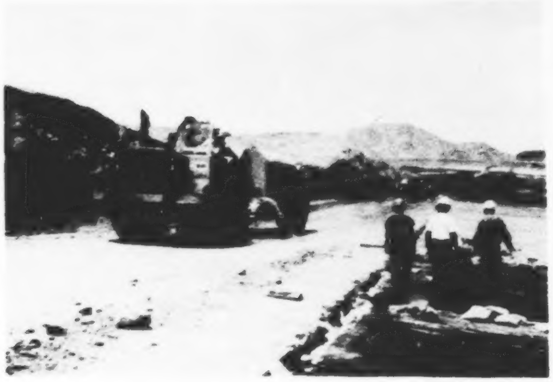

Figure 56. Dust control on haul roads.

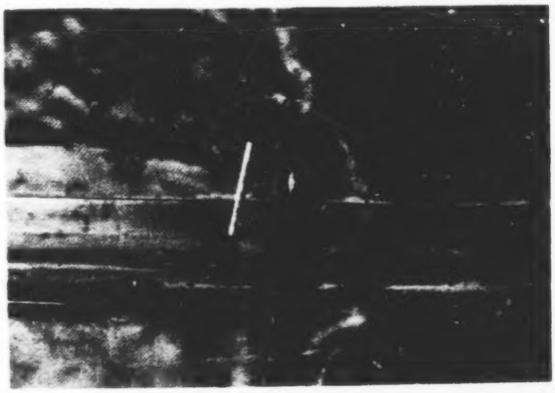

Figure 57. 'Blocking.'

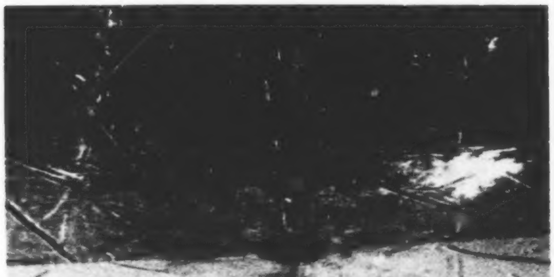

Figure 58. Repair of 'Blocking.'

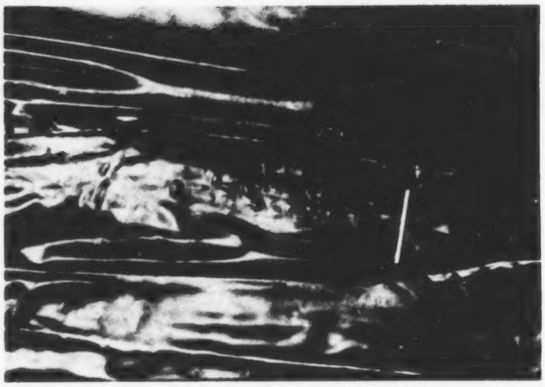

Figure 59. Blistering from solvent evaporation.

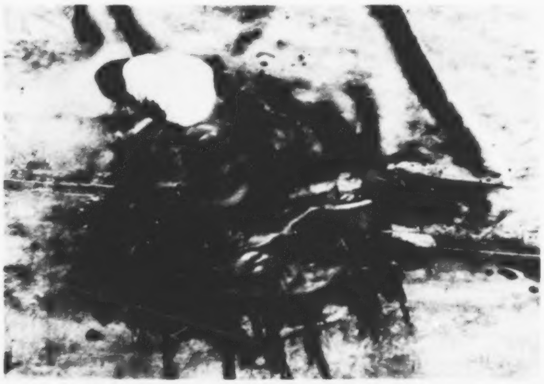

Figure 60. Patch over field seam.

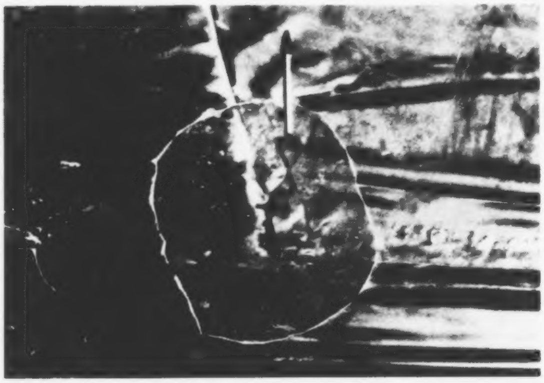

Figure 61. Patch over field seam.

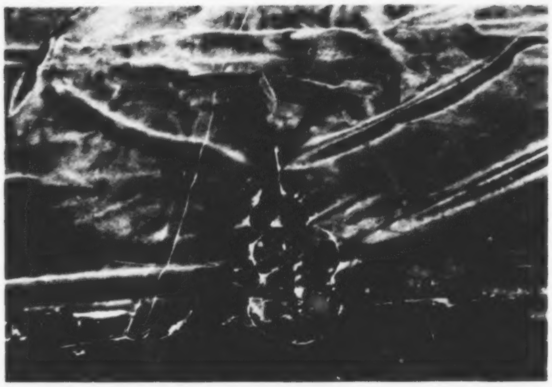

Figure 62. Multiple patching should be avoided.

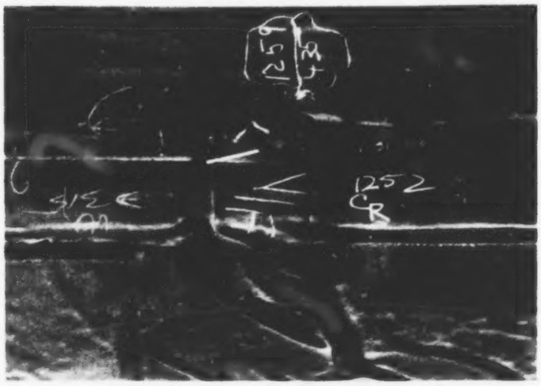

Figure 63. Planned quality control inspection.

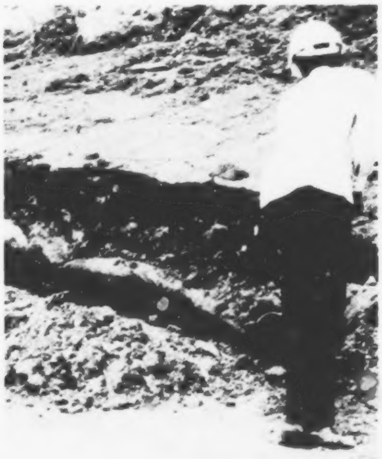

Figure 64. Exposing edge of liner for expansion.

Figure 65. Flap to be used for future expansion of liner.

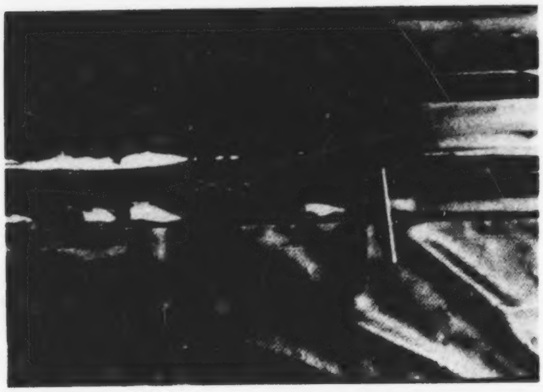

Figure 68. Two materials 'married' together for cost effective design.

Figure 66. Flap sealed into place (shown on left).

Figure 69. Monitoring well casing.

Figure 67. Shows the use of two liner materials.

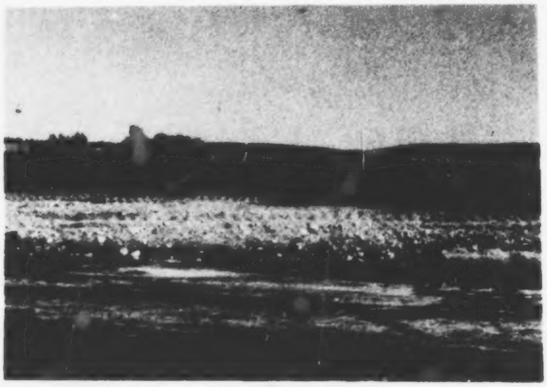

Figure 70. Completed landfill cover.

Figure 71. Surface cover for a landfill showing gas vent pipes.

Figure 72. Surface runoff diversion dam shown in upper left hand corner.

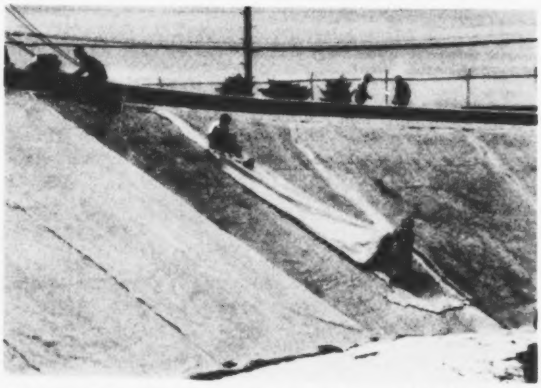

Figure 74. Placement of filter fabric over differential settling crack in concrete.

Figure 73. Shows use of a membrane and soil liner.

INTERACTION OF SELECTED LINING MATERIALS WITH VARIOUS HAZARDOUS WASTES - II

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Matrecon, Inc.
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ABSTRACT

Results of the exposure under several conditions of selected lining materials to typical hazardous wastes for periods up to three years are presented. These exposure tests include:

1. One-sided exposure of a square foot of each of 12 lining materials under one foot of six different wastes.
2. Immersion testing of 12 types of polymeric membrane lining materials in water and in nine wastes.
3. Tests of nine different thermoplastic materials fabricated into bags and filled with wastes to assess their compatibility and the permeability of the membranes.
4. Outdoor exposure testing of specimens of membrane materials exposed on racks and in 12 tubs containing various wastes.

INTRODUCTION AND OBJECTIVES

In view of the nation's great dependence upon groundwater as a source of potable water, the need to protect the groundwater from pollution by wastes placed on land for storage or disposal is quite obvious.

Placing a highly impermeable man-made layer or liner below the disposal site offers a means of intercepting the flow of pollutant from the wastes and thus protecting the groundwater.

This study was undertaken in 1975 to determine the state-of-the-art of liner technology and to assess experimentally a broad range of promising lining materials which were available at that time. The principal objectives of the study are:

1. To determine the effects of exposing a selected group of lining materials to various hazardous wastes over an extended period of time.

2. To determine the durability of and the cost effectiveness of utilizing synthetic membranes, various admix materials, and native soils as liners for hazardous wastes storage and disposal sites.

3. To estimate the effective lives of 12 lining materials exposed to six types of industrial nonradioactive hazardous waste streams under conditions which simulate those encountered in holding ponds, lagoons, and landfills.

In this study, the lining materials that are being studied are a native soil, two treated bentonite clays, soil cement, hydraulic asphaltic concrete, an asphaltic membrane, and a wide range of commercial or developmental flexible polymeric membranes. The polymers used in the manufacture of these membranes are polyvinyl chloride, chlorinated polyethylene, chlorosulfonated polyethylene, ethylene propylene rubber, neoprene, butyl rubber, an elasticized polyolefin, and a thermoplastic polyester. The nine hazardous wastes selected for exposure testing included strong acids, strong bases, oil refinery tank bottom wastes, lead wastes from gasoline, saturated and unsaturated hydrocarbon wastes, and a pesticide waste.

Specimens of the lining materials are exposed to wastes under a variety of circumstances which simulate conditions that might be encountered in actual service. These tests consist of one-sided exposure, two-sided exposure, outdoor exposure, and composite exposure to weather and wastes.

Results have been reported in two previous symposia: At Tucson, Arizona[1], in 1976 and at San Antonio, Texas, in 1978[2]. Additional details are given in an interim report on the project[3].

In this paper we present the current results of exposure testing of various lining materials, particularly the polymeric membrane materials. Data on the effects to liners of exposure to wastes of up to three years duration are included.

EXPERIMENTAL APPROACH AND METHODOLOGY

To meet the principal objectives of this project, we selected a range of promising lining materials which have low permeability and exposed them to a series of typical hazardous wastes under different conditions which we felt would be aggressive to lining materials. The effects of the exposure were measured as a function of time by such means as weight change, change in physical properties, seepage through the primary liner specimens and permeation through membranes.

Details of our approach which is reviewed briefly below are given in References 1, 2, and 3.

The lining materials included both flexible polymeric membranes and various admixed types, e.g. soils, soil cements, asphaltic concrete, and membranes. All were selected on the basis of their having low permeability to water and having a history of use in the impoundment of water and various industrial wastes and chemicals.

Polymeric membranes based upon eight different polymers were selected for the exposure testing. The polymers include butyl rubber, chlorinated polyethylene, chlorosulfonated polyethylene, elasticized polyolefin, ethylene propylene rubber, neoprene, polyester elastomer, and polyvinyl chloride. All of the membrane lining materials were commercial products except the polyester elastomer which was included because of its reportedly high resistance to oily wastes. The admix materials included compacted native fine grain soil, hydraulic asphalt concrete, asphalt emulsion membrane, modified bentonite, and soil cement.

Nine hazardous wastes were selected from the petroleum, chemical, and pesticide industries for use in this test program. They include two strongly acidic wastes, two strongly alkaline wastes, a lead waste which was a blend of three lead wastes, three oily wastes, and a pesticide waste. These examples were felt to be typical of the range of wastes and all except the pesticide waste contain constituents which were felt to be aggressive toward lining materials. The properties of these wastes are given in Tables 1 and 2, taken from Reference 2. In addition to these wastes, several additional test fluids were incorporated in the test program for assessing membrane liners. The test fluids included deionized water, a 5% aqueous solution of sodium chloride, a highly ionic hazardous waste containing minor amounts of organic chemicals and a saturated solution of tributyl phosphate in deionized water. The latter solution was kept saturated by means of a reservoir of tributyl phosphate.

The principal exposure test used in this project consisted of exposing one square foot liner specimens in cells, such as shown in Figure 1, under one foot of the wastes.

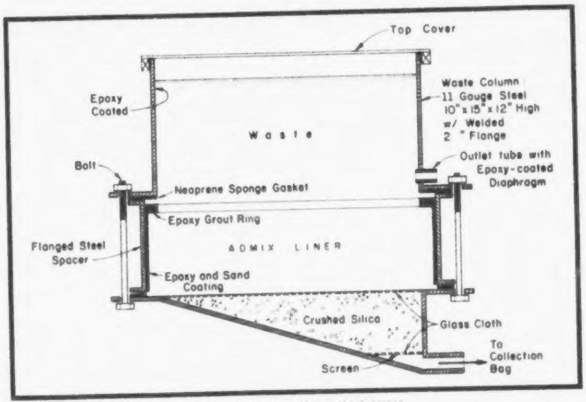

Figure 1. Exposure cell for admix liners.

TABLE 1. WASTES IN EXPOSURE TESTS

Phases

Type of Waste	Name	Organic Phase I	Water Phase II	Solids Phase III
Acidic	"HFL"[a]	0	100	0
	"HNO_3, HF, HOAC"[b]	0	100	0
Alkaline	"Slopwater"[a]	0	100	0
	"Spent caustic"[b]	0	95.1	4.9
Lead	"Low lead gas washing"))Blend[b]	10.4	86.2	3.4
	"Gasoline washwater")	1.5?	89.1?	-
Oily	"Aromatic oil"[b]	100	0	0
	"Oil Pond 104"[b]	89.0	0	11.0
	"Weed oil"[a]	20.6	78.4	-
Pesticide	"Weed killer"[b]	0	99.5	0.5

[a] In immersion tests only.
[b] In both primary exposure and immersion tests.

TABLE 2. WASTES IN EXPOSURE TESTS

pH, Solids, and Lead

Type of waste	Name	pH Water phase	Solids, %		Lead, ppm
			Total	Volatile	
Acidic	"HFL"	4.8	2.48	0.9	-
	"HNO_3, HF, HOAC"	1.5	0.77	0.12	-
Alkaline	"Slopwater"	12.0	22.43	5.09	-
	"Spent caustic"	11.3	22.07	1.61	-
Lead	"Low lead gas washing"	7.2	1.52	0.53	34
	"Gasoline washwater"	7.9	0.32	0.17	11
Oil	"Aromatic oil"	-	-	-	-
	"Oil Pond 104"	-	*ca*. 36	*ca*. 31	-
	"Weed oil"	7.5	1.81	1.00	-
Pesticide	"Weed killer"	2.7	0.78	0.46	-

This schematic drawing illustrates the cell designed for the admix specimens. Such cells were constructed with spacers between the upper part of the cell, which contains the test fluid, and the base in which is placed a coarse silica sand. Membrane specimens were tested in the same type of cell, except that a spacer is not needed.

The original program called for 12 lining materials to be exposed to six wastes; however, it was soon apparent that many of the combinations of liners and wastes were incompatible and liner failure would occur in relatively short periods of time. A preliminary screening test was performed on various combinations of liners and wastes and specific combinations were then selected for the long term tests. The selected combinations are shown in Table 3. Two cells of each combination were set up to allow for two exposure periods. The first set of liner specimens were recovered and tested after approximately one year of exposure. These results were reported at the San Antonio Symposium[2]. The second set of specimens are being removed and test results obtained to date are reported in this paper.

In order to extend the number of wastes and liners, the tests in the primary cells were supplemented by the immersion testing of 12 liners in nine wastes. Specimens of membrane liners were placed in the additional test fluids given above.

In the immersion test procedure, small slabs of the lining materials were hung in the test fluids that were in the primary cells. Not only did this allow an expanded exposure test, but it also allowed exposure of two sides of the liner to the waste. Such a procedure accelerates the effects of exposure and allows the specimens hung in the wastes which stratify to show the effect of stratification of the waste. This condition is in contrast to that in the primary cell in which the liner is at the bottom of the cell and only one side is exposed to the waste.

Inasmuch as many of the liners for ponds and lagoons which are used in the storage or disposal of hazardous wastes are exposed to the weather, outdoor exposure testing of some of the membrane liners was performed. Two types of tests were included. In the first samples of the liner materials were exposed in an undeformed condition on a rack and the effects of weather were observed by removing specimens at different times and testing and, in the second, the liners are simultaneously exposed to the weather and to the wastes. This was accomplished through the use of small tubs which were lined with the material being tested and the tubs filled with waste. This type of test simulates open-service and also allows the liner materials to be draped over sharp corners which simulates some conditions encountered in service.

As most of the wastes contain water, a separate study was made of the effect of water upon polymeric membrane lining materials at room temperature and at 70°C. For this test we followed ASTM D751, in which the water absorption is observed as a function of time.

A test method developed in our project on liners for landfills was adapted for liners for hazardous wastes. In this test bags of heat-sealable membranes were fabricated and filled with waste or other test fluids such as salt water. The bags were sealed and immersed in deionized water. The permeabilities of the membrane to water and to pollutants are determined by observing respectively the change in weight of the bag and the measurement of pH and electrical conductivity of the deionized water. Due to osmosis water should enter the bag and ions and dissolved constituents should leave the bag.

THE PRIMARY LINER SPECIMENS

Polymeric Membrane Liners

All of the flexible polymeric membranes survived the exposure testing, except the polyester elastomer which failed on exposure to the nitric acid waste. This material completely lost its elongation and cracked in the cell at the edges of the liner. The nitric acid waste caused several of the cells to leak due to corrosion of the steel cell through pinholes in the epoxy coating at welds between the cell walls and the flanges.

In the case of the admix materials, there was seepage through the soil, soil cement, asphalt concrete, and bentonite

TABLE 3. MATERIALS TESTED AS LINERS IN THE PRIMARY EXPOSURE CELLS CONTAINING VARIOUS WASTES

Material	Liner No.[a]	Type of compound[b]	Extractables, %	Waste					
				Pesticide	HNO_3	Spent caustic	Lead	Oil 104	Aromatic oil
Flexible polymeric membranes:									
Butyl rubber (Butyl)	57R[c]	VZ	6.4	T	T	T	T	[d]	[d]
Chlorinated polyethylene (CPE)	77	TP	9.1	T	T	T	T	T	[d]
Chlorosulfonated polyethylene (CSPE)	6R[c]	TP	3.8	T	T	T	T	T	T
Elasticized polyolefin (ELPO)	36	TP	5.5	T	T	T	T	T	T
Ethylene propylene rubber (EPDM)	26	VZ	18.2	T	T	T	T	T	T
Chloroprene rubber (Neoprene)	43	VZ	13.9	T	[d]	T	T	T	[d]
Polyester elastomer (Polyester)	75	TP	2.7	T	T	T	T	T	T
Polyvinyl chloride (PVC)	59	TP	35.9	T	T	T	T	T	T
Admixes:									
Compacted fine grain native soil				T	d	T	T	T	T
Soil cement				T	[d]	T	T	T	T
Treated bentonite with sand:									
A				T	[d]	[d]	T	T	T
B				T	[d]	[d]	[e]	[e]	[e]
Hydraulic asphalt concrete				T	T	T	T	[d]	[d]
Emulsified asphalt membrane				T	[d]	T	T	[d]	[d]

[a] Identification number assigned by Matrecon.

[b] Type of compound, i.e. vulcanized (VZ) or thermoplastic (TP).

[c] R = Fabric reinforced.

[d] Combination of liner and waste was eliminated in the screening test.

[e] Spacers not available.

liners. The seepage through the soil did not contain the waste which had been placed on the soil. It was the fluid from the pores within the soil itself. As the soil contained considerable salt when it was placed (it had been dredged from San Francisco Bay), the fluid which seeped also had a high salt content.

The hydraulic asphalt concrete failed below the nitric acid waste, principally because of the incorrect choice of aggregate. The acid consumed much aggregate and hardened the asphalt considerably eventually resulting in the concrete leaking. Another asphalt concrete liner which was placed beneath the lead waste failed. This waste contained considerable low molecular weight oily material which the asphalt absorbed and became "mushy".

Mostof the cells containing pesticide, nitric acid waste, spent caustic waste and lead waste have been dismantled and the liner specimens have been tested. The cells containing the two oily wastes are in the process of being dismantled and the liners tested.

The membrane liners that were removed from the cells were photographed, inspected visually, and subjected to the following tests:

- Determination of volatiles and extractables.
- Tensile properties in machine and transverse directions.
- Hardness.
- Tear strength in machine and transverse directions.
- Puncture resistance.
- Seam strength.

The results related to the volatiles and extractables, ultimate elongation and modulus, are presented in Tables 4 and 5.

Determining the volatiles and extractables of the exposed liner supplies information with respect to the amount of waste that is absorbed by the liner and the amount of the original compound that is leached out during the exposure. The volatiles were run first by determining the loss in weight of a 2 inch diameter disk heated for two hours at 105°C. The extractables were determined on specimens that had been devolatilized by heating two hours at 105°C. The appropriate solvent was used in order to extract the nonpolymeric fraction without dissolving the polymer.

The volatiles test was also used to verify the direction of the grain of the membrane which was introduced during manufacture. (On heating polymeric liners shrink more in the machine direction.) Some physical properties are significantly affected by grain direction, a factor which was not considered in the preparation of some of the early specimens.

Elongation which is an important property in the functioning of many rubber and plastic products appears an important property for liners. The loss of elongation in service either by loss of plasticizer or by excessive swelling could result in breakage of a membrane, since it would not tolerate the extension for which it was designed. The stress at 100% elongation is a measure of the stiffness or modulus of a rubber or plastic compound. It is affected by the amount of swelling that takes place and by crosslinking or oxidation that might take place in the rubber. This property is related to hardness.

As shown in Table 4, all of the materials that were exposed Absorbed volatile material, primarily water, and, in the case of the lead waste, some low molecular weight hydrocarbons. The two liners which absorbed the least amount of volatile material were the elasticized polyolefin and the polyvinyl chloride membranes. The rubber liners tended to absorb more; the neoprene and the chlorinated polyethylene absorbed the most.

In most cases, the "extractables", of the exposed liners were higher than the extractables of the respective unexposed liner material. Exceptions were the polyvinyl chloride, the chlorinated polyethylene, and, to a minor extent, the neoprene, all of which had been immersed in lead waste. The plasticizers in these materials leached into the wastes resulting in a lower extractables contents.

The elongation data in Table 5 show almost complete loss of elongation by the

TABLE 4. VOLATILES[a] AND EXTRACTABLES[b] OF PRIMARY POLYMERIC MEMBRANE LINER SPECIMENS AFTER EXPOSURE TO SELECTED WASTES

Liner data		Compound data		Volatiles, % Waste and exposure time in days (d)					Extractables, % Waste and exposure time in days (d)			
Polymer	No.[c]	Type[d]	Extractables, %	Unexposed	Pesticide 1260 d	HNO_3 1220 d	Caustic 1250 d	Lead 1340 d	Pesticide 1260 d	HNO_3 1220 d	Caustic 1250 d	Lead 1340 d
Butyl	57R	VZ	6.4	0.29	4.8	11.5	1.4	3.5	7.6	8.7	7.9	7.9
CPE	77	TP	9.1	0.00	7.9	13.2	2.8	19.2	9.4	10.6	9.1	7.2
CSPE	6R	TP	3.8	0.29	9.7	7.2	5.8	11.4	5.4	4.6	3.8	6.0
ELPO[e]	36	TP	5.5	0.15	...[f]	5.3	...[f]	1.5	...[f]	7.1	...[f]	8.1
EPDM	26	VZ	18.2	0.50	6.3	12.0[g]	1.3	5.3	25.2	22.8[g]	24.0	26.0
Neoprene	43	VZ	13.9	0.45	13.6	...	5.7	17.5	16.1	...	13.7	12.2
Polyester	75	TP	2.7	0.26	2.9	7.4[h]	0.9	1.7	5.8	13.5[h]	3.3	5.4
PVC	59	TP	35.9	0.26	3.6	...[f]	1.8	4.4	33.4	...[f]	35.6	22.5

[a] Percent weight loss after 2h @ 105°C.

[b] After devolatization in air oven for 2h @ 105°C.

[c] No. = Serial number of liner set by Matrecon; R = Reinforced with a fabric.

[d] Type = Vulcanized (VZ) or thermoplastic (TP).

[e] ELPO = Elasticized polyolefin.

[f] Specimens still under exposure to waste.

[g] Exposure time = 1150 days.

[h] Exposure time = 509 days.

polyester elastomer in the nitric acid waste. The other lining materials retained most of their respective elongations. The CSPE showed the greatest loss other than the polyester elastomer, retaining 68% of its original elongation.

The S-100 modulus of the neoprene liner immersed in the pesticide and the lead wastes showed significant losses. These losses of modulus are the result of excessive absorption of water and components of the wastes. The pesticide waste had a low ion concentration which resulted in high absorption of water. The lead waste contained oily material which was absorbed by the neoprene.

There were significant increases in stiffness (S-100 modulus) by the PVC liner exposed to the pesticide and the caustic wastes and by the CSPE which was exposed to the caustic waste. These changes in stiffness within an exposure period of less than three and one-half years indicate that, on extended periods of time, there will be considerable hardening.

Admix Liner Materials

As shown in Table 3, five types of admix materials are being studied in this project:

- Compacted fine-grain native soil.
- Soil cement.
- Modified bentonite in sand.
- Hydraulic asphalt concrete.
- Membrane based on emulsified asphalt on a nonwoven fabric.

Because of the incompatibility of some of the wastes with particular admix materials, several combinations were deleted. These deletions are shown in the table. The only liner material that was placed below the acid waste was the hydraulic asphalt concrete. Neither of the two oily wastes was placed on the asphaltic liners; however, the lead waste, which contained a light oily fraction, was placed on these liners. The performance of the individual admix liners is discussed below:

Compacted Fine-grain Soil--

All of the wastes, except the nitric acid waste, were placed above the compacted fine-grain soil liner. Seepage below all of the liners took place. The amount of seepage was measured and the respective pH, conductivity, and percent total solids were determined. The following observations are made with respect to the seepages through the soil liners:

- The rateof seepage is 10^{-8} to 10^{-7} cm sec^{-1} which compares favorably with the permeability of the soil measured in the laboratory permeameter. There is some variation in the amount of seepage collected below the liner which may reflect permeability differences, perhaps due to density of the soil.

- The fluids being collected after more than three years of exposure still continue to be essentially neutral and to have high solids content (mostly salt) and electrical conductivity.

- There is a downward trend in solids content of the seepages collected under the pesticide and lead wastes, but the seepage under the spent caustic waste continues to be 23% solids.

One set of the soil liners has been removed and tested.

The permeability of a specimen taken from the cell containing the soil and the aromatic oil waste was determined using the standard "back-pressure" procedure. The sample was collected from a depth of seven to ten inches below the surface of the soil, i.e. from that part of the soil which was not penetrated by the oil. The three consecutive values obtained were: 1.83×10^{-8}, 2.43×10^{-8}, and 2.60×10^{-8} cm sec^{-1}. These figures indicate the low permeability of the soil, which had a bulk density of 1.318 g cm^{-3} and a saturation degree of 101%.

Trace metals analyses were made of the soils which were below the lead waste, Oil 104, and the aromatic oil. The testing included determination of pH and heavy metal content (cadmium, chromium, copper, magnesium, nickel and lead) on samples

TABLE 5. RETENTION OF ULTIMATE ELONGATION[a] AND S-100 MODULUS[b] OF PRIMARY POLYMERIC MEMBRANE LINER SPECIMENS ON EXPOSURE TO SELECTED WASTES

Liner data		Compound data			Ultimate elongation, % retention Waste and exposure time in days					S-100 modulus, % retention Waste and exposure time in days			
Polymer	No.[c]	Type[d]	Extractables, %	Original elongation,[e] %	Pesticide 1260 d	HNO_3 1220 d	Caustic 1250 d	Lead 1340 d	Original S-100,[f] psi	Pesticide 1260 d	HNO_3 1220 d	Caustic 1250 d	Lead 1340 d
Butyl	57R	VZ	6.4	70	77	419	142	108	...	...	...	...	...
CPE	77	TP	9.1	405	90	88	115	84	900	114	84	132	72
CSPE	6R	TP	3.8	235	88	83	68	81	645	118	112	199	118
ELPO[g]	36	TP	5.5	665	...[h]	96	...[h]	106	875	...[h]	103	...[h]	110
EPDM	26	VZ	18.2	450	103	79[i]	95	106	360	88	70[i]	109	80
Neoprene	43	VZ	13.9	320	84	...	95	75	460	54	...	96	62
Polyester	75	TP	2.7	575	87	<1[e]	87	90	2585	96	...	110	88
PVC	59	TP	35.9	385	93	...[h]	95	106	960	144	...[h]	170	107

[a] Ultimate elongation = The average of the values in both machine and transverse directions.
[b] S-100 modulus = The average of the values in both machine and transverse directions of the stress at 100% elongation.
[c] No. = The serial number of liner set by Matrecon.
[d] Type = Vulcanized (VZ) or thermoplastic (TP).
[e] Original elongation = Ultimate elongation of unexposed material.
[f] Original S-100 = S-100 modulus of unexposed material.
[g] ELPO = Elasticized polyolefin.
[h] Specimens still under exposure to waste.
[i] Exposure time = 1150 days.
[j] Exposure time = 509 days.

collected at different depths in the cells.

With the exception of the liner with spent caustic, the pH of the Mare Island soil liner was not significantly altered by the wastes. The pH of these samples was in the range of 7.0 to 7.6; the ratio soil: solution was 1:2 with 0.01 N $CaCl_2$ being the equilibration solution.

In the case of the spent caustic, the pH values were around 9.0 for samples collected in the first two to three centimeters, which concurs with our previous findings that, over the exposure period of 30 months, the wetting front of the wastes penetrated the soil to a depth of only three to five centimeters.

The heavy metals distribution, as indicated by the analysis, shows, in the case of the lead, only a very shallow contamination of the soil. Similar results were obtained on all six of the heavy metals in the case of the soil below the Oil 104 waste.

Soil Cement--

All of the wastes except the acid waste were placed on the soil cement liner. No seepage occurred through the liner during the 30 months of exposure.

One set of the soil cement lining materials was recovered after 625 days of exposure to the various wastes and the individual linings have been cored and tested for compressive strength. In all cases, compressive strength of the exposed soil cement was greater than that of the unexposed material. There was some blistering of the epoxy asphalt coating which was applied to one-half the surface of each specimen.

Modified Bentonite and Sand--

Two types of modified bentonites were used as liners in ten cells. One type allowed somewhat less seepage than the other. There was measurable seepage in seven of the ten cells and one failed allowing the waste (Oil 104) to come through the liner.

Irrespective ofthe type of waste above the liner, the quality of the seepage was not greatly different among the samples collected. The seepage collected below the pesticide waste of both types of modified bentonite liners were similar.

When the spacers containing the bentonite-sand were sampled, it was found that there had been considerable channeling of the wastes into these liners. There was no channeling at the walls of the spacer.

We conclude that this liner is probably not satisfactory for these types of of waste. (We prepared these liners as directed by the suppliers.) The use of a soil cover on the bentonite layer to produce an overburden would probably reduce the channeling effect.

Hydraulic Asphalt Concrete--

Liner specimens of hydraulic asphalt concrete were placed under four of the wastes. Excluded were the oily wastes.

This lining material functioned satisfactorily under the pesticide and spent caustic wastes, but failed beneath the nitric acid waste. However, the failure arose primarily from the failure of the aggregate which contained calcium carbonate; also the asphalt tended to harden considerably.

In the case of the lead waste, the asphalt absorbed much of the oily constituents of the waste and became "mushy". There was some staining of the gravel below the asphalt liner.

The second cell containing the hydraulic asphalt concrete and the lead waste is still functioning without seepage.

Membrane Based on Emulsified Asphalt and Nonwoven Fabric--

This membrane was placed under only three of the six wastes: pesticide, spent caustic, and lead wastes. The acid waste was deleted because of the severe hardening the acid waste caused the asphalt, and the oil wastes were deleted because of the high mutual solubility of the asphalt and the wastes.

The asphalt membrane functioned satisfactorily with the pesticide and spent caustic wastes; however when the cell containing the lead waste was dismantled the gravel below the liner was wet and stained brown. This result indicates that some seepage took place.

IMMERSION TESTING OF THE MEMBRANE LINER MATERIALS

To expand the matrix of information relating to the compatibility of membrane liners and wastes, samples of additional liner materials were immersed in nine different wastes, including the six wastes that were used in the primary test program. This test study was further expanded to include 22 liner materials and plastics and 13 wastes and test fluids.

In this paper, results on the immersion testing are presented for 12 liner materials in eight wastes. Data include exposures of approximately 2.2 years. The test was designed to immerse specimens of sufficient size to perform most of the same tests that had been performed on the primary samples. Missing from the immersion study was the seam adhesion test. The specimens, each six by eight inches, were weighed and measured prior to exposure and weighed and measured when removed from the waste after which they were tested for volatiles and extractables, tensile, tear, and puncture strength. The same type of data as were presented for the primary liners are reported for the immersion test specimens. Tables 6, 7, and 8 present data on weight changes during the immersion, and "volatiles" and "extractables" of the exposed specimens. Data on the physical properties, ultimate elongation, and S-100 modulus are presented in Tables 9 and 10.

In all tables, the data are arranged by waste and liner. Also included in the tables are data on the liner compounds, such as the type of compound, that is, whether it is thermoplastic or vulcanized, the amount of extractable material in the original compound, and data for the pertinent property measured on the unexposed lining. The weight gains, extractables, and volatiles are presented in percent, the elongation and modulus data are presented as a retention of the property after the exposure period.

As shown in Table 6, most of the liner materials that were exposed in the wastes gained weight, particularly those that were immersed in wastes which contained oily components. Even among the oily wastes the amount of swelling, or weight change, is determined by the type of hydrocarbons they contain, i.e. their molecular weight and aromaticity. The aromatic oil and the weed oil caused the greatest degree of swelling. Both of these wastes are aromatic; furthermore, the weed oil contains low molecular hydrocarbons. The swelling was so great in the case of the CPE and CSPE liners that the specimens disintegrated or swelled to the point where they could not be effectively tested for physical properties.

In several instances, the PVC liner specimens actually lost weight. A loss in weight reflects leaching of the plasticizer and possibly the loss of absorbed material by syneresis. Such losses generally result in reduced elongation and substantially increased modulus.

Inasmuch as a considerable amount of the weight of the immersed specimens consists of volatile components, volatility tests were run, the results of which are presented in Table 7. Again, the results show a substantial volatiles content, particularly in the wastes which are basically aqueous. The waste which caused the lowest volatiles in the liners and also the lowest weight increase was the spent caustic. The pesticide waste caused comparatively high weight gain and volatiles content; the aromatic oil, which resulted in high weight increases, yielded relatively low volatiles because it is nonvolatile.

The nonvolatile extractable components in the immersed liner were determined following the volatility tests with the results presented in Table 8. Part of the extractables are from the original compound and part absorbed from the waste. Comparisons can be made with the extractables in the original compound to determine the amount of nonvolatile waste the liner absorbed and the amount of compounding oils and plasticizers which had leached out of the compounds. A precise ratio, however, requires further analysis of the extracted fraction.

Of particular interest is the significant loss of plasticizer of the PVC liners immersed in the lead, Oil 104, and weed oil wastes. Also of interest is the higher extractables of most of the liner materials which were immersed in oil-containing wastes. The liners that were in the predominantly aqueous wastes generally did not lose plasticizer. It can be assumed in long-term exposure that the soluble components of a compound will eventually leach into the waste and that some waste compo-

TABLE 6. ABSORPTION OF WASTE BY POLYMERIC MEMBRANE ON IMMERSION IN SELECTED WASTES
(Data in Weight Percent)

		Data on liner compound		Waste and immersion time in days (d)							
Polymer	No.[a]	Type[b]	Extract-ables, %	Pesticide 807 d	HNO_3 751 d	HF 761 d	Spent caustic 780 d	Lead 786 d	Oil 104 752 d	Aromatic oil 761 d	Weed oil 809 d
Butyl	44	VZ	11.8	1.6	3.8	3.7	0.8	28.7	103.9	31.2	64.2
CPE	77	TP	9.1	12.7	19.9	12.9	1.1	118.9	36.9	226.4	ND[c]
CSPE	6R[d]	TP	3.8	17.3	10.0	9.0	4.3	120.7	49.5	105.2	368.4
CSPE	55	TP	4.1	15.7	10.9	7.7	3.3	116.2	55.0	110.5	347.5
ELPO[e]	36	TP	5.5	0.5	7.6	1.1	0.6	17.0	28.9	29.4	38.1
EPDM	83R[d]	TP	18.2	4.5	4.2	3.1	1.6	24.8	26.5	19.8	84.4
EPDM	91	VZ	23.6	20.4	50.9	23.9	1.3	34.7	84.7	34.2	76.2
Neoprene	90	VZ	21.5	11.4	17.4	12.0	1.5	59.1	26.3	142.6	89.3
Polyester	75	TP	2.7	4.2	6.4	2.0	1.5	7.4	8.5	16.6	14.7
PVC	11	TP	33.9	5.1	22.1	18.1	0.4	-1.5	-10.4	18.5	15.3
PVC	59	TP	35.9	1.0	-6.1	0.9	-0.9	7.4	-0.5	28.9	24.7
PVC	88	TP	33.9	1.6	28.2	14.3	1.1	-5.2	-9.8	14.1	25.2

[a] No. = the serial number of liner set by Matrecon.
[b] Type = vulcanized (VZ) or thermoplastic (TP).
[c] ND specimen was lost; some indication that it dissolved in the waste.
[d] R = fabric reinforced.
[e] ELPO = elasticized polyolefin.

TABLE 7. VOLATILES[a] CONTENT OF FLEXIBLE POLYMERIC LINERS ON IMMERSION IN SELECTED WASTES

(Data in percent loss of weight)

		Data on liner compound			Waste and immersion time in days (d)							
Polymer	No.[b]	Type[c]	Extract-ables, %	Volatiles (unexposed)[d] %	Pesticide 807 d	HNO_3 751 d	HF 761 d	Spent caustic 780 d	Lead 786 d	Oil 104 752 d	Aromatic oil 761 d	Weed oil 809 d
Butyl	44	VZ	11.8	0.28	3.0	3.8	2.9	6.9	15.3	9.8	3.3	19.2
CPE	77	TP	9.1	0.00	8.6	20.4	8.1	1.6	42.2	5.2	ND[e]	ND[f]
CSPE	6R[g]	TP	3.8	0.29	10.8	10.4	7.6	4.2	3.3	20.2	6.1	50.7
CSPE	55	TP	4.1	0.42	7.9	9.1	7.1	3.6	1.1	10.0	4.8	39.7
ELPO[h]	36	TP	5.5	0.15	0.45	7.2	1.3	0.6	9.5	3.1	1.5	16.4
EPDM	83R[g]	TP	18.2	0.31	4.89	3.1	2.8	2.2	13.9	8.5	4.4	24.1
EPDM	91	VZ	23.6	0.34	15.6	22.6	23.6	1.2	18.5	11.8	4.2	33.4
Neoprene	90	VZ	21.5	0.27	7.26	13.7	10.5	2.9	23.6	6.3	3.9	28.9
Polyester	75	TP	2.7	0.26	1.75	28.0	3.8	1.3	6.1	2.1	3.4	9.5
PVC	11	TP	33.9	0.15	30.9	22.6	18.3	0.6	16.1	2.7	3.6	17.1
PVC	59	TP	35.9	0.26	40.1	10.6	3.0	1.5	12.7	3.3	4.6	16.1
PVC	88	TP	33.9	0.17	3.51	23.2	13.1	1.2	11.5	4.3	3.5	24.1

[a] "Volatiles" content is the loss in weight of a specimen of liner (unexposed or exposed) on air-oven heating for 2 hours at 105°C.

[b] No. is the serial number of liner assigned by Matrecon for identification.

[c] Type of compounds: vulcanized (VZ) or thermoplastic (TP).

[d] Volatiles content of unexposed specimens of liners.

[e] ND = no data obtained because the sample was too badly deteriorated to test.

[f] Immersion sample was lost. Some indication that it dissolved in the waste.

[g] R = fabric reinforced.

[h] ELPO = elasticized polyolefin.

TABLE 8. EXTRACTABLES OF FLEXIBLE MEMBRANE LINERS AFTER IMMERSION IN WASTE AND DEVOLATILIZING IN OVEN FOR 2 HOURS AT 105 °C
(Date in weight percent based upon the devolatilized specimen)

	Data on liner compound			Waste and immersion time in days (d)							
Polymer	No.	Type	Extractables, %	Pesticide 807 d	HNO_3 751 d	HF 761 d	Spent caustic 780 d	Lead 786 d	Oil 104 752 d	Aromatic oil 761 d	Weed oil 809 d
Butyl	44	VZ	11.8	...	11.1	10.6	10.9	17.1	40.3	27.2	15.2
CPE	77	TP	9.1	...	12.0	10.2	9.2	16.6	19.2	ND[c]	ND[c]
CSPE	6R[d]	TP	3.8	...	3.8	3.8	3.8	4.6	16.3	45.4	19.0
CSPE	55	TP	4.1	...	4.0	3.6	4.2	3.7	15.9	59.8	16.1
ELPO	36	TP	5.5	...	6.2	5.1	5.5	6.9	17.8	23.3	8.1
EPDM	83R[d]	TP	18.2	...	17.6	17.1	18.0	21.2	22.2	27.2	18.7
EPDM	91	VZ	23.6	...	25.4	22.4	22.9	30.0	43.5	38.4	25.4
Neoprene	90	VZ	21.5	...	19.2	19.6	20.8	19.2	23.9	58.5	7.6
Polyester	75	TP	2.7	...	10.8	3.3	2.7	3.3	6.5	16.6	6.1
PVC	11	TP	33.9	35.4	32.3	32.7	33.9	17.3	18.0	40.6	21.1
PVC	59	TP	35.9	34.9	23.3	34.0	35.8	27.9	28.0	47.6	30.1
PVC	88	TP	33.9	31.7	33.2	31.1	32.5	17.9	14.8	38.5	20.1

[a] No. = The serial number of liner set by Matrecon.
[b] Type = Vulcanized (VZ) or thermoplastic (TY).
[c] Specimen was lost; some indication that it dissolved in the waste.
[d] R = Fabric reinforced.
[e] ELPA =Elasticized polyolefin.

TABLE 9. PERCENT RETENTION OF S-100 MODULUS[a] BY FLEXIBLE POLYMERIC LINERS ON IMMERSION IN SELECTED WASTES
(Data in Percent of S-100 of the Unexposed Liner)

		Data on liner compound			Waste and immersion time in days (d)							
Polymer	No.[b]	Type[c]	Extract-ables, %	Original S-100,[d] psi	Pesticide 807 d	HNO₃ 751 d	HF 761 d	Spent caustic 780 d	Lead 786 d	Oil 104 752 d	Aromatic oil 761 d	Weed oil 809 d
Butyl	44	VZ	11.8	310	88	72	93	91	57	45	56	39
CPE	77	TP	9.1	900	102	69	116	126	18	45	ND[e]	ND[f]
CSPE	6R[g]	TP	3.8	945	124	67	126	170	88	88	73	ND[e]
CSPE	55	TP	4.1	880	122	71	113	167	93	89	85	ND[e]
ELPO[h]	36	TP	5.5	875	122	99	112	116	80	79	76	57
EPDM	83R[g]	TP	18.2	810	94	84	109	100	44	54	58	ND[e]
EPDM	91	VZ	23.6	340	90	58	100	100	73	58	60	67
Neoprene	90	VZ	21.5	560	77	63	104	121	38	70	40	27
Polyester	75	TP	2.7	2585	111	-	117	105	92	95	76	78
PVC	11	TP	33.9	1280	118	104	106	121	102	207	131	52
PVC	59	TP	35.9	960	135	262	129	128	91	152	112	47
PVC	88	TP	33.9	1735	100	70	83	99	97	172	123	45

[a] S-100 modulus is the average of the values obtained in each the machine and transverse directions.
[b] No. is the serial number of liner assigned by Matrecon for identification.
[c] Type of compounds: vulcanized (VZ) or thermoplastic (TP).
[d] Original S-100 modulus is the averaged S-100 of the liner membrane before immersion in the waste.
[e] ND = no data obtained because the sample was too badly deteriorated to test.
[f] Immersion sample was lost. Some indication that it dissolved in the waste.
[g] R = fabric reinforced.
[h] ELPO = elasticized polyolefin.

TABLE 10. PERCENT RETENTION OF ULTIMATE ELONGATION[a] BY FLEXIBLE POLYMERIC LINERS ON IMMERSION IN SELECTED WASTES
(Data in Percent Retention)

		Data on liner compound			Waste and immersion time in days (d)							
Polymer	No.[b]	Type[c]	Extractables, %	Original elongation,[d] %	Pesticide 807 d	HNO_3 751 d	HF 761 d	Spent caustic 780 d	Lead 786 d	Oil 104 752 d	Aromatic oil 761 d	Weed oil 809 d
Butyl	44	VZ	11.8	445	109	110	93	94	111	54	102	71
CPE	77	TP	9.1	405	94	88	81	87	92	92	ND[e]	ND[f]
CSPE	6R[g]	TP	3.8	235	82	126	93	72	65	79	77	ND[e]
CSPE	55	TP	4.1	280	79	104	94	74	60	68	52	ND[e]
ELPO[h]	36	TP	5.5	665	95	97	96	91	84	88	90	78
EPDM	83R[g]	TP	18.2	255	128	135	109	111	157	145	155	ND[e]
EPDM	91	VZ	23.6	490	101	97	86	106	98	52	100	56
Neoprene	90	VZ	21.5	415	101	87	68	83	91	77	62	65
Polyester	75	TP	2.7	575	89	1	90	84	101	96	87	96
PVC	11	TP	33.9	350	103	86	86	97	104	85	76	107
PVC	59	TP	35.9	385	96	65	93	86	101	96	78	96
PVC	88	TP	33.9	330	98	86	89	100	105	78	82	107

[a] Ultimate elongation = the average of the values in both machine and transverse directions.
[b] No. = the serial number of liner set by Matrecon.
[c] Type = vulcanized (VZ) or thermoplastic (TP).
[d] Original elongation is the averaged ultimate elongation of the liner membrane before immersion in the waste.
[e] ND = no data because sample was too deteriorated to test.
[f] ND specimen was lost; some indication that it dissolved in the waste.
[g] R = fabric reinforced.
[h] ELPO = elasticized polyolefin.

nents will swell the lining materials. The net effect will determine the overall degree of swell of the lining materials and the effect upon physical properties, particularly elongation and stiffness.

In Tables 9 and 10 the results of the retention of elongation and modulus are presented in comparison with the original values obtained on unexposed samples of the respective liners. The effect upon different liners varies considerably with the waste, polymer, and liner compound. Of particular interest are the effects upon the PVC compounds which vary among the three PVC's and among the wastes. The nitric acid waste caused a significant increase in the stiffness of one PVC membrane but a substantial loss in another. Two of the oils, Oil 104 and the aromatic oil, increased the modulus; weed oil reduced the modulus. Again, these effects are a function of the aromaticity of the oil and its molecular weight.

The retention of elongation, a property which appears to relate to the functioning of a liner, varies considerably with the liner and the waste. In several cases, the elongation of the liner was reduced by almost 50%, a value which in many rubber products is considered to be critical to utility. Low retention values were also encountered with CSPE and EPDM in oily wastes. The polyester elastomer became nonserviceable in contact with nitric acid waste early in the exposure period; it had an elongation of less than 1% of its original elongation within a few days of exposure. One PVC liner lost 35% of its elongation, which reflects a substantial loss of plasticizer. PVC's in other wastes are also showing weight losses which could be indicative of long-term problems with this type of liner where high oily wastes are used. However, if polymeric liners are placed into a "proper" waste, the loss of plasticizer could be offset by the absorption of the waste to yield compatible combinations, which would not result in excessive hardening and loss of elongation.

WATER ABSORPTION OF POLYMERIC LINERS

As most of the wastes contain water which most polymeric materials absorb to varying degrees, the water absorption of a series of liners is being measured for extended periods of time, in accordance with ASTM D570. The results of the tests at 1113 days at room temperature and at 70°C are presented in Table 11. The change in weight varies considerably with the material and with the temperature of test. At room temperature, the weight change ranges from + 0.9% for elasticized polyolefin to + 67% for a neoprene liner material. At 70°C, the change was a loss of 4% for the elasticized polyolefin to excessive swelling and disintegration of the specimen of butyl liner. Other liners which showed excessive swelling at the higher temperatures were the two neoprenes, the chlorinated polyethylene, and the chlorosulfonated polyethylene. One of the two polyvinyl chloride liners in the test swelled or increased in weight 125%, whereas the second increased only 26%; however, the liner which increased the lesser amount had become quite stiff, indicating that it had lost plasticizer. Therefore, in considering the weight gain of a lining material on exposure to a waste, the loss of oils and plasticizers within the compound should also be considered. Furthermore, the swelling at the higher temperatures, although rapid, cannot always be used as a measure of the level of weight increase at lower temperatures. For example, the butyl that disintegrated at 70°C, swelled 11% at room temperature, and the CSPE which swelled almost 440% at 70°C, swelled about 21% at room temperature. On the other hand, a neoprene liner swelled 350% at 70°C and 44% at room temperature.

OUTDOOR EXPOSURE OF POLYMERIC MEMBRANE LINERS

The second of three sets of specimens of 11 polymeric membranes that were exposed to the weather have been recovered and tested after 745 days of exposure. These specimens are six-inch squares cut from the sheeting and mounted at 45° on a rack facing southward on the roof of our laboratory in Oakland, California. On removal from the rack, the samples are cleaned, weighed, and their dimensions measured, after which selected physical properties are measured. The effects of the exposure on the ultimate elongation and the weight of the material are presented in Table 12. As discussed above, the retention of elongation is a measure of the rubberiness of the membrane that is retained and the change in weight is an indication of the loss of volatiles, e.g. plasticizer, and possibly of the degradation of the polymeric compound. All materials remained rubbery and serviceable,

TABLE 11. CHANGE IN WEIGHTS[a] OF POLYMERIC MEMBRANE LINERS IMMERSED IN WATER FOR 1113 DAYS
(Percent weight change)

Liner data		Compound data		Immersion temperature	
Polymer	No.[b]	Type[c]	Extractables, %	Room	70°C
Butyl	57R	VZ	6.4	10.9	–[d]
CPE	77	TP	9.1	16.9	179.9
CSPE	6R	TP	3.8	20.8	438.2
ELPO	36	TP	5.5	0.9	-4.2
EPDM	8	VZ	23.4	3.5	12.6
EPDM	26	VZ	23.0	3.9	21.1
Neoprene	43	VZ	13.7	67.2	387.7
Neoprene	82	VZ	13.4	44.0	350.0
Polyester	75	TP	2.7	1.6	-0.8
PVC	11	TP	33.9	1.7	126.3
PVC	59	TP	35.9	4.5	26.2

[a] Test method ASTM D570. Data are the average of three values.
[b] Matrecon identification number; "R" indicates liner has fabric reinforcement.
[c] Type = Vulcanized (VZ) or thermoplastic (TP).
[d] Specimen disintegrated.

TABLE 12. OUTDOOR EXPOSURE OF POLYMERIC MEMBRANE LINERS ON ROOF RACK
Effects upon the Ultimated Elongation[a] and Weights of the Membrane Specimens

Liner data		Thickness, mils	Compound data			Retention of elongation, %		Change in weight, %	
Polymer	No.[b]		Type[c]	Extractables, %	Ultimate elongation,[d] %	343 d	745 d	343 d	745 d
Butyl	57R	34	VZ	6.4	75	41	125	-1.89	-2.79
CPE	77	29	TP	9.1	325	100	92	-0.99	-2.27
CSPE	6R	32	TP	3.8	240	63	52	+0.64	+0.91
ELPO	36	23	TP	5.5	675	96	96	-0.72	-1.55
EPDM	8	62	VZ	23.4	520	94	89	-2.02	-3.09
EPDM	26	39	VZ	23.0	440	89	94	-1.69	-2.71
Neoprene	43	34	VZ	13.7	330	76	68	-1.80	-2.96
Neoprene	82	60	VZ	13.4	390	80	64	-0.53	-1.17
Polyester	75	7	TP	2.7	340	89	88	-2.50	-8.32
PVC	11	30	TP	33.9	365	100	93	-1.36	-8.40
PVC	59	33	TP	35.9	370	92	88	-1.45	-6.66

[a] Elongation of the liner measured in the machine direction. Retention of elongation on exposure after 343 and 745 days given in % of the original elongation.
[b] Matrecon identification number. "R" indicates liner is fabric reinforced.
[c] Type: Compound is vulcanized or is thermoplastic.
[d] Ultimate elongation of unexposed liner.

which indicates that they would be satisfactory for several years more. However, the CSPE and neoprene membranes lost significant elongation, probably the result of crosslinking which had taken place during exposure. All three of these compounds increased substantially in modulus which, in rubber technology, is related to crosslinking of the rubber. The butyl rubber liner has given erratic results, probably due to its low initial elongation, i.e. 75%, and to the fabric reinforcement.

All of the specimens lost weight except that based on CSPE. The greatest losses were incurred by the two PVC specimens and by the polyester elastomer specimen. The loss of weight by the PVC specimens is no doubt caused by loss of plasticizer; however, the loss did not cause a significant loss of physical properties. The loss in weight by the polyester which does not contain plasticizer may reflect polymer degradation.

In addition to the small slabs of liners which are being exposed to the weather on the roof rack, we have 12 small tubs lined with various polymeric membranes and filled with wastes. In this test, nine different lining materials are being exposed to four different wastes. Of the 12 tubs, only one has failed, a tub lined with elasticized polyolefin and containing Oil 104 waste. The specimen cracked at a sharp fold in the area which is exposed at times to both the oil and the air. This liner also showed significant swelling.

The butyl liner is showing cracking at sharp bends. All of the liners containing oil exhibit some swelling. Also, the polyvinyl chloride liner containing the nitric acid waste is hardening.

Exposure is being continued and the tubs will be dismantled when they fail and the specimens tested.

BAG TEST FOR ASSESSING MEMBRANE LINER MATERIALS

The bag test described above, which was developed originally for use on the landfill project, has been applied to a variety of thermoplastic polymeric materials and the wastes being used in this project. The initial tests were made with the thermoplastic materials because they could be fabricated into bags with ease by heat sealing. Some of these bags have now been exposed more than 1000 days. This test method continues to be a very promising one for assessing the long-term performance of membrane lining materials.

We showed previously that the bags containing the wastes actually increased in weight, indicating the flow of water into the bags through osmosis, as shown in Table 13. The long-term tests now show that some ionic material is diffusing through the liners into the deionized water in the outer bags. Table 14 presents the interpolated or estimated times to reach an electrical conductivity of 1000 μmho for slopwater and nitric acid, both of which are concentrated wastes. The data show the higher permeability of the PVC lining materials as compared to CPE, CSPE, elasticized polyolefin, and polybutylene. Of particular interest is the low permeability of the elasticized polyolefin and the polybutylene, both of which are partially crystalline materials. Table 15 presents the results of thethermoplastic membranes tested with 5% sodium chloride solution. The data again show the greater permeability of the PVC with respect to the CSPE and the elasticized polyolefin, which is the most impermeable of the three. These bags have now been taken out of test and physical properties of the bag wall materials have been measured. The results show that, within the 1150 days of exposure, there is some loss in elongation and an increase in the stiffness of the membranes.

DISCUSSION

At this point in the project, when we are recovering and testing specimens which have been exposed to wastes under some test conditions for more than three years, we can make a few observations which we feel will be helpful in the choice of lining materials for impounding specific wastes.

There does not appear to be any single lining material now commercially available which is suitable for long-term impoundment of all wastes. Generally, wastes that are highly ionic, contain salts, strong acids, or strong bases, can be aggressive to soils, soil cement, aggregate, hydraulic asphaltic concrete, and to some of the membranes, particularly those containing plasticizers. Wastes which have organic components can be aggressive toward the membrane liners and toward asphaltic materials. However, there

TABLE 13. RELATIVE PERMEABILITIES OF POLYMERIC MEMBRANE LINING MATERIALS IN BAG TEST WITH THREE WASTES

Average Flux into the bag in grams per square meter per day x 10^{-2}[a]

Polymer	Liner no.	Nominal thickness, mils	HNO_3 waste	Spent caustic	Slop water
CPE	86	22	78.2	26.3	190.7[b]
CSPE	85	33	67.8	36.3	49.2
ELPO[c]	36	23	2.54	3.80	18.4[d]
Polybutylene	98	7.5	2.98	7.94	13.6
PVC	19	22	32.4	78.8	325.0
PVC	88	20	64.2	65.9	118.8[e]

[a] Exposure time is 552 days unless otherwise noted.
[b] Bag failed at 450 days.
[c] Elasticized polyolefin.
[d] Bag failed at 300 days.
[e] Bag failed at 40 days.

TABLE 14. PERMEABILITY OF THERMOPLASTIC POLYMERIC MATERIALS IN OSMOTIC BAG TEST

Time in Days for Electrical Conductivity of Water in Outer Bag to Reach 1000 μmho

	Wall of inner bag			Waste in inner bag	
Polymer	Liner No.[a]	Thickness, mils	Extractables, %	HNO_3 waste	"Slopwater"
CPE	86	20	...	200	420
CSPE	85	33	...	500	510
ELPO[b]	36	22	5.5	300	>1000
PB[c]	98	7	...	600	>1000
PVC	19	20	38.9	70	200
PVC	88	20	33.9	110	160

[a] Matrecon identification number.
[b] Elasticized polyolefin.
[c] Polybutylene.

TABLE 15. BAG TEST OF THERMOPLASTIC MEMBRANES[a]

Bags Filled with 5% NaCl Solution

Polymer	CSPE	ELPO[b]	PVC
Liner No.[c]	6	36	59
Thickness, mils	32	23	33
Volatiles content of exposed bag wall, %	8.7	0.38	0.90
Change in weight of bag plus waste, %	2.6	0.71	0.38
Change in weight of fluid in bag during exposure, %	0.95	0.76	0.38
Conductivity of water in outer bag, μmho	585	34	4500
Retention of physical properties, %:			
Elongation	95	100	94
S-100	106	119	120

[a] Exposure time: 1150 days (164 weeks).
[b] Elasticized polyolefin.
[c] Matrecon identification number.

is considerable variation in the compatibity of wastes and liners. In particular, the oily wastes cause swelling and loss of physical properties in the membrane liners and the asphaltic materials.

It is quite apparent, therefore, that compatibility studies must be performed prior to the selection of the liners for handling specific wastes and that, once the selection has been made and the site lined, the waste that is being impounded should be monitored closely to insure that only proper waste is added. In making these studies, contact of samples of the liner under consideration and the waste to be impounded should be as long a time as possible. Our tests show that, in many cases, no leveling off with time occurs in the effects of the waste on the membrane. Such behavior means that, for long-term exposures, there can be a continuing change of the liner with time.

In developing a new liner material for use in the lining of waste disposal sites, it is quite obvious that the new material should be tested under a variety of enviromental conditions. Furthermore, it would appear desirable to consider composite types of liners involving two or more materials for use in impounding more aggressive and polluting types of wastes.

In the case of the polymeric membrane liners, some of the more useful tests and properties which appear to be promising for assessing the suitability of a given liner for use with a given waste are:

1. The measurement of swelling of the membrane materials in the wastes or in the leachate of the wastes.

2. The loss of elongation with time of the polymeric membranes when in contact with the waste or its leachate.

3. The use of a bag test for measuring the compatibility of the liners and the waste and the permeability of the liner to the constituents of the waste.

There is still a need to correlate these experimental tests with long-term exposures in order that laboratory tests can be used to assess liners and predict their long-term performance in service. Such correlation requires observation of liners in actual service under extended periods of time.

ACKNOWLEDGMENTS

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ASSESSMENT OF PROCESSES TO STABILIZE ARSENIC-LADEN WASTES

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ABSTRACT

Industrial solid waste containing arsenic was treated with many proprietary and generic fixation processes to evaluate the processes' ability to retard the leaching of arsenic. This evaluation was achieved by performing several types of laboratory leaching tests. Several processes were found to reduce arsenic leaching rates by at least four orders of magnitude. A concluding discussion shows that fixation can be economically competitive with other legal methods of hazardous waste disposal. Several barriers to implementation are identified.

INTRODUCTION

Many industrial residues containing arsenic are presently held in long-term storage because of the lack of an acceptable disposal method. Other similar residues are disposed of on land, but the design, construction and operation of secured landfills that can protect water resources from arsenic contamination are often very difficult and expensive. This paper describes investigations conducted to determine whether fixation is a useful technique that can expand the options for safe disposal of arsenic-containing wastes.

Previously published papers(1,2) and a draft final report(3) have presented details of the experimental work. Many of these details are, therefore, mentioned only briefly in this paper, which addresses the more interpretive phases of the work.

EXPERIMENTAL

As the above-cited papers and report describe, three wastes were selected for investigation based on a national survey of arsenic producers and users. The wastes differed widely from each other in physical and chemical properties. Only one waste - filter cake from the purification of food-grade phosphoric acid - is discussed in this paper, because the data from that waste demonstrate several important points.

The waste was treated by a variety of fixation processes. These included processes performed by commercial ventures, those developed at universities, and some generic processes that were performed in the JBF laboratories. Leaching tests were conducted with all products. This paper discusses the results for six vendor processes. Products were molded by all vendors into cylinders 7.5 cm in diameter and approximately 20 cm long.

Two types of leaching tests are discussed here: a long-term shake test and a modified Extraction Procedure (EP). The version of the EP was current at the time of this work, but differs from that later proposed(4) by EPA for identification of hazardous wastes under Section 3001 of the Resource Conservation and Recovery Act (RCRA).

The shake test was used to assess the long-term behavior of intact specimens in contact with water. Shake test steps are briefly described:

1. Cut a cylindrical slice of approximately 100 g from the fixed monolithic product (usually about 2 cm thick).
2. Support the sample so that all sides are exposed to water in a glass jar. Add CO_2-saturated

distilled water in the ratio 10 ml H_2O:g sample. Raw waste tests involved a 50-g sample and 1 liter water.

3. Oscillate jar at 60 1-in. strokes /hr.

4. Sample and replace water every 48 hrs. Analyze sample for components of interest.

5. Repeat Step (4) for up to two months.

The version of the EP used was as follows:

EQUIPMENT

1. An agitator that, while preventing stratification of sample and extraction fluid, also ensures that all sample surfaces are continuously brought into contact with well-mixed extraction fluid.

2. Equipment suitable for maintaining the pH of the extraction medium at a selected value.

PROCEDURE

1. Weigh a representative sample of the waste to be tested. Separate sample into liquid and solid phases by either centrifugation, followed by filtration of the liquid through a 0.4- to 0.5-μ filter media, or by pressure filtration using a 0.4- to 0.5-μ filter having a surface area of at least 0.5 cm^2/g of sample. Save the liquid for further use.

2. Grind the solid material, if necessary, to pass through a 9.5 mm (3/8") standard sieve.

3. The solid material is taken and added to eight times its weight of deionized water. The pH of the solution is then adjusted to pH 5 with 1:1 acetic acid or 1 N sodium hydroxide. Samples are to be determined electrometrically following standard calibration procedures.

4. Samples are to be maintained at room temperature during extraction. They are to be agitated for 24 ± 0.5 hr with pH to be maintained during leaching within the range 4.9-5.2. The preferred method of maintaining pH is with automatic titration. If the necessary equipment is not available, manual procedures can be employed.

5. At the end of the 24-hr extraction period the solution is filtered as in Step 1. The filtrate is then adjusted with deionized water so that its volume is 10 times the initial weight of solid sample [v(cc)/w(g)]. The liquid is combined with the original liquid phase and the solid reextracted with fresh extractant as in steps 3 and 4.

6. At the end of the second extraction period the mixture is filtered, the concentration adjusted as in Step 5, and the liquid phase combined with that from the previous separations. This combined liquid, and any precipitate that later forms, is designated as the toxicant extraction procedure eluate.

pH ADJUSTMENT PROCEDURES

Automated: Follow manufacturer's instructions as to procedures for instrument calibration and operation.

Manual: This section prescribes procedure to use if extractant pH is maintained manually.

1. Calibrate pH meter in accord with manufacturer's specifications.

2. Adjust pH of solution to 5.

3. Manually adjust pH of solution at 15, 30 and 60 minutes, increasing the interval if the pH did not have to be adjusted more than 0.5 pH units since the previous adjustment.

4. Continue procedure for a period of not less than 6 hrs.

5. Final pH after a 24-hr period must be within the range 4.9-5.2.

6. If the conditions of Step 5 are not met, continue pH adjustment at approximately 1-hr intervals for a period of not less than 4 hrs.

Other leaching tests were performed and are reported elsewhere(1-3); space does not permit coverage of all results in this paper.

ANALYSES

Arsenic analyses were performed on a Perkin-Elmer Model 372 atomic absorption spectrophotometer. Digestions for assay analysis of the stabilized residues were conducted in a mixture of hydrofluoric, hydrochloric, and nitric acid within a tightly sealed Teflon®* vessel.

DISCUSSION OF RESULTS

Forms of Presentation

The leaching data from the shake tests are presented in two forms: the maximum arsenic concentration (usually found at the first sampling/water change event), and the cumulative mass of arsenic leached after repetitive sampling and analysis. This second form of data reporting has been used in studies on other industrial wastes(5), and on radioactive wastes(6,7). The mass of pollutant leached is considered in relation to that initially present in the sample, and the fractional mass leached in each time period is expressed cumulatively. It is also useful for comparing data from differently configured specimens to normalize the data with the volume:surface ratio. Therefore, the parameter

$$\frac{\Sigma a_n}{A_0} \cdot \frac{V}{S}$$

Where
Σa_n = cumulative mass of arsenic leached in n periods
A_0 = mass of arsenic initially present in sample
V = sample volume
S = sample apparent surface area

has been used to express leaching behavior in shake tests. Godbee and Joy(6) showed the usefulness of this parameter in connection with diffusion theory; they used the expression

$$\frac{\Sigma a_n}{A_0} \cdot \frac{V}{S} = 2\left(\frac{De}{\pi}\right)^{1/2} t^{1/2}$$

where
De = effective diffusivity
t = time
and other symbols have been defined above.

Plotting

$$\frac{\Sigma a_n}{A_0} \cdot \frac{V}{S} \text{ versus } t^{1/2}$$

should yield a straight line with slope equal to $2(De/\pi)^{1/2}$ if diffusion of arsenic to the surface of the solid is the limiting factor in leaching. The effective diffusivity can then be computed from the value of this slope.

Results

Data from the two leaching tests used are shown in Table 1. For the shake test, two forms of results are shown: the maximum arsenic concentration (usually observed in the first sampling) and De, the effective diffusivity. Several observations result from review of these data:

1. The extraction procedure on crushed samples was not well correlated with the shake test. The least successful product according to the EP was the most successful according to the shake test.

2. The two forms of shake test results are consistent with one another; inferences about process ranking based on initial arsenic release were confirmed by the long-term release rate based on effective diffusivity, De.

3. The long-term release rate is a more sensitive indicator of success than the other parameters shown. While concentrations varied by a factor of 100 to 200, effective diffusivity values varied by a factor of 17,000.

This last inference is demonstrated by a diffusion plot, as shown in Figure 1.

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*Registered trademark of E.I. du Pont de Nemours and Company, Inc., Wilmington, Delaware

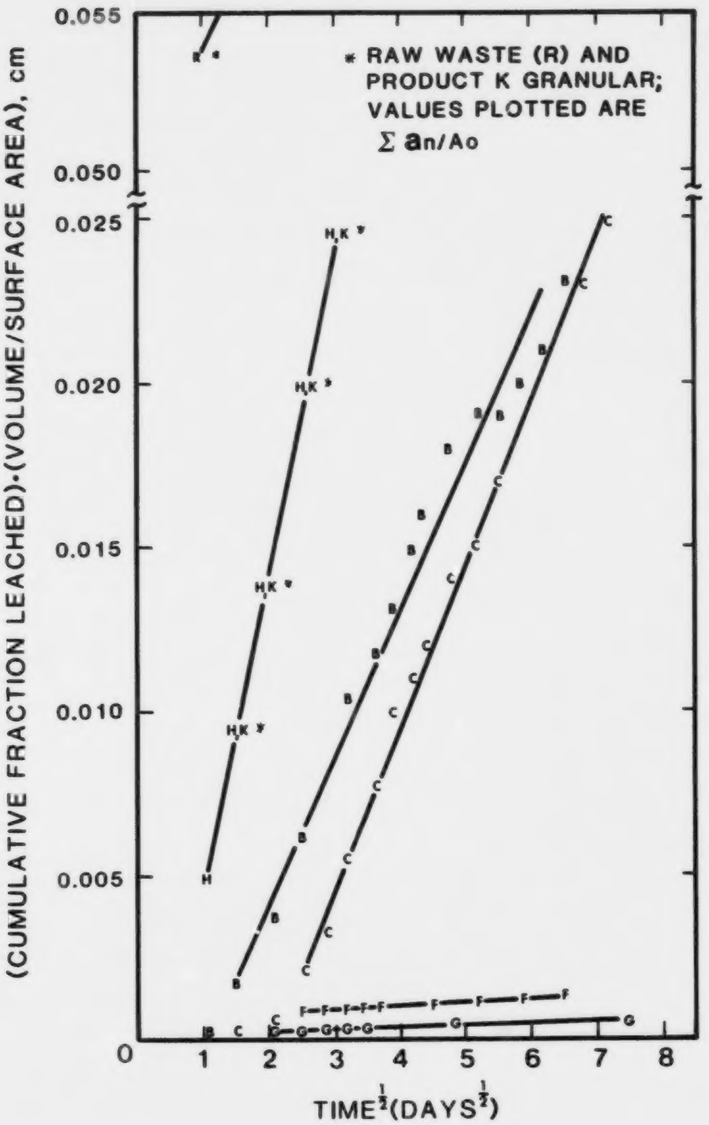

Figure 1. Diffusion Plot, Waste No. 2. Plotted letters are codes for processes. Volume/surface area ratios were 0.6 to 0.7.

TABLE 1. RESULTS OF LEACHING TESTS

Process	EP Result (mg/ℓ As)	Shake Test Results Maximum As Concentration (mg/ℓ)	De (cm^2/day)
B	127	2.1	1.8×10^{-5}
C	5.2	3.4	1.9×10^{-5}
F	1.7	1.1	2.6×10^{-8}
G	162	0.2	1.1×10^{-8}
H	97	7.9	1.9×10^{-4}
K	43	4.0	*
Raw Waste	41	40	*

* = Granular

Computations of De were based on the slopes from this plot.

ECONOMICS

Normally, generators of hazardous waste will seek to minimize disposal costs within regulatory constraints on environmentally acceptable disposal methods. EPA, in its Proposed Rules on Hazardous Waste(4), briefly related the concept of fixation to environmental acceptability in the context of the Extraction Procedure (EP); it stated that the Extraction Procedure "is designed to encourage the chemical or physical 'fixing' of waste so that its constituents are no longer available to be leached out." This view of fixation requires complete success in making the waste non-hazardous. Whether such success was achieved in this study is uncertain because the officially proposed EP differs from that used here. If one assumes that some processes used here would have been successful in rendering wastes non-hazardous (perhaps with more tailoring of processes to suit the wastes), some economic generalizations can be derived.

Cost estimates provided by fixation vendors for the processes used in this study varied widely, were accompanied by many caveats, and were not correlated with processes' success. For discussion purposes, however, a typical approximate cost can be set at approximately $100/kkg (metric ton) of waste. Literature values(8, 9, 10) for costs of transport and disposal of hazardous wastes at distant sites (e.g. 500 miles to an acceptable site, which is common for industries in New England) indicate that costs for this option can exceed $100/kkg. Thus, fixation and disposal at a nearby conventional municipal landfill appears cost competitive.

Another way to view fixation is under the "degree of hazard" concept. Comments on the Proposed Rules have frequently disputed the classification of all wastes into only two groups: "hazardous" and "non-hazardous". The point has been made by many commenters that several classes of "degree of hazard", each with appropriate disposal requirements, may be more cost effective and environmentally sound. If the "degree of hazard" concept were implemented, hazardous waste generators would have the opportunity to demonstrate that wastes, even though not totally benign, could be disposed of with techniques less sophisticated than those required for very hazardous wastes. For example, wastes that had been fixed to reduce their leaching potential to an intermediate extent might be disposed of at an intermediate technology landfill. Cases would probably arise where this opton would have lower costs and no more environmental hazard than either of the options described in the preceding paragraph.

BARRIERS TO IMPLEMENTATION

Any evaluation of the market potential of a technology such as fixation requires an unbiased analysis of a complex set of technical, economic and other factors. The foregoing discussion has shown that fixaton has high potential for expanding the options for safe disposal of hazardous wastes. Although these general findings cannot be applied to every waste/site combination, the fixation option appears sufficiently attractive to stimulate questions about why it is not used more frequently.

Among the most important reasons for the lack of widespread use of fixation are:

- Delays in official promulgation of hazardous waste regulations;
- Uncertainty about the long-term stability of fixed products;

Uncertainty about future definitions of "hazardous". Disposal is normally a perpetual commitment, but industry is concerned that what is legal today may be found unwise through future research.

All three of these reasons are based on inadequate knowledge. Active research programs can improve the state of knowledge, the basis for sound regulations, and the decisions of hazardous waste generators.

CONCLUSIONS

Commercially available fixation processes offer a wide range of effectiveness in reducing the leaching of arsenic from waste discussed here. Some processes reduced leaching rates by more than four orders of magnitude relative to raw wastes and some less effective processes. Several commercial processes can achieve this level of improvement. Inferences about whether a given process was "successful" should be site-specific, in the context of a total disposal system design. Leaching tests with granular samples provide different inferences from tests with monolithic samples.

The costs of fixation may be offset by the opportunity to dispose of adequately fixed wastes at sites that may not require sophisticated control and monitoring. For example, the cost to transport and dispose of untreated hazardous wastes at distant, secure disposal sites can be greater than the cost of fixation and disposal at a nearby site with less stringent requirements.

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FIELD INVESTIGATION OF CONTAMINANT LOSS FROM CHEMICALLY STABILIZED SLUDGES

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ABSTRACT

The movement of contaminants from treated industrial sludges placed at four disposal sites was examined. Test borings were made through the treated sludges into the soil beneath and into surrounding, uncontaminated soils. Measurements of selected chemical constituents in nitric acid digests from shallow soil samples collected immediately below the treated sludges and from soil samples collected at comparable elevations in surrounding soils were compared using the Mann-Whitney U Test. Soils beneath treated auto assembly wastes disposed at two locations showed elevated levels of manganese, sodium, and selenium. Soils beneath treated electroplating waste showed elevated levels of iron, sodium, mercury, and nickel. At one location where treated oil refinery waste was disposed no significant soil contamination was detected. Even in contaminated soils the levels of constituents determined were well within the ranges reported for natural soils.

INTRODUCTION

This report is an extension of earlier work on the effects of landfilled treated or solidified wastes or surrounding groundwater and soil.[5] An earlier report covered the investigation of groundwater chemistry and the physical properties of the soils at treated industrial waste disposal sites. The current investigation examines effects of treated wastes on the chemical composition of surrounding soils.

In the earlier study groundwater analyses from four disposal sites where treated industrial wastes had been placed showed little contamination that could be related to the disposed wastes.[5] Waste containment could be attributed to either the treatment process or to soil attenuation. The goal of the present investigation is to determine if increased levels of potential contaminants from the treated wastes are present in the soil under the disposal sites. The presence of elevated levels of contaminants in the soils is attributed to release of these materials from the solidified/stabilized wastes.

Thirty-five million metric tons (roughly 77 billion pounds) of hazardous wastes must be disposed in the country each year. In many cases reuse or incineration is not appropriate and the material must be landfilled.[3] Solidification/stabilization may greatly reduce the potential hazard associated with landfilling.

In the present investigation, four sites where treated industrial sludges containing electroplating, metal finishing or refinery wastes had been placed are examined. A summary of the major characteristics of each site is given in Table 1. All of the sites are located in humid areas where the production of leachate from the waste is probable. None of the landfills are lined or had any secondary containment facilities. All of the sites contain treated sludges that have appreciable metal content (Table 2). The treatment process used involved the addition of cementitious materials to the sludges to produce a soil-like material. All four sludges were treated by the same processor.

Soil samples were obtained from under the disposal sites and from similar elevations surrounding the site.

TABLE 1. SUMMARY OF CHARACTERISTICS OF FOUR SITES SELECTED

Characteristic	Site W	Site X	Site Y	Site Z
Geographic area within the U. S.	Central	North Central	North Central	South Central
General geologic setting	Glacial Drift	Glacial Outwash	Pleistocene - Lake Terrace	Deltaic - Fluvial Deposits
Mean annual rainfall	102 cm	93 cm	88 cm	117 cm
Mean annual air temperature	$12^{\circ}C$	$11^{\circ}C$	$10^{\circ}C$	$21^{\circ}C$
Nature of waste	Paint, putty	Electroplating	Paint, putty	Refinery sludge
Major pollutants detected in sludge analyses	B, Cr, Fe, Pb, Mn, Ni, Zn	Cd, Cr, Cu, Mn, Na, Zn	Cr, Fe, Pb, Mn, Zn	Pb, Mn, and phenol
Liner used below fill	None	None	None	None
Thickness of waste	1.22-3.05m (avg. 2.14m)	0.91-1.22m (avg. 1.07m)	Thin*	1.83-3.20m (avg. 3.79m)
Nature of material in unsaturated zone	Sandy clay	Sandy clay	Clayey sand	Clay
Thickness of unsaturated zone	3.05-8.60m (avg. 5.60m)	2.16-2.93m (avg. 2.41m)	1.46-11.80m (avg. 8.79m)	1.04-6.63m (avg. 3.79m)
Average hydraulic conductivity below waste	1.1×10^{-7} cm/sec	3.45×10^{-7} cm/sec	2.63×10^{-4} cm/sec	4.2×10^{-7} cm/sec
Character of covering material	None	None	None	Clay
Average thickness of cover	0.0	0.0	0.0	0.5m
Dates of emplacement of fixed sludge	1974	1973	1974*	1974
Type of operation	Diked fill	Diked fill	Fill	Diked fill and cover

* Fixed waste was placed on the ground in April and May 1974; but, the major portion of the fixed material was removed to a landfill in Jaunary 1975 when the area was regraded.

The soil samples were digested in concentrated nitric acid and the digests were analyzed for selected metals. A nonparametric statistical test, the Mann-Whitney U test[6,7] (one-tailed, level of significance = 0.10) was used to determine if the soils directly under the disposal site were significantly higher in metal content than the surrounding soils.

MATERIALS AND METHODS

Sampling Procedures

Eight to ten borings were put down to the water table at each site. The locations of the borings at each disposal area are given in Figures 1-4. All boring was done with a truck-mounted, 16.8-cm diam hollow stem auger. Soil samples were obtained by drilling to the selected depth with a central plug in place in the auger. To obtain a sample the central plug was withdrawn from the auger and a thin-walled tube sampler (Hvorslev sampler) or a split-spoon sampler was lowered into the hollow-stemmed auger and driven or pushed into the soil below the auger cutting tip. This technique is a standard system for foundation testing.[1,2] Care was taken to clean the samplers before use so as to avoid contamination of the soil samples. Soil samples were extruded from the sampler on the surface,

TABLE 2. CONCENTRATIONS OF MAJOR CHEMICAL CONTAMINANTS IN THE FIXED SLUDGE AT EACH SITE*

Constituent	Site W (mg/kg)**	Site X (mg/kg)	Site Y (mg/kg)	Site Z (mg/kg)
B	43	95	10	6.4
Cd	4.5	105	0.1	1.8
Cr	230	1600	30	960
Cu	28	1650	18	130
Fe	47,000	4000	23,500	16,800
Pb	40	20	40	3300
Mn	850	110	572	275
Ni	75	50	30	25
Se	1	1.3	0.62	0.83
Na	350	1281	2000	1340
Zn	1300	450	200	520
Hg	0.05	0.20	0.02	6.2

* Data obtained analyses of sludge samples.
** On a dry wt basis.

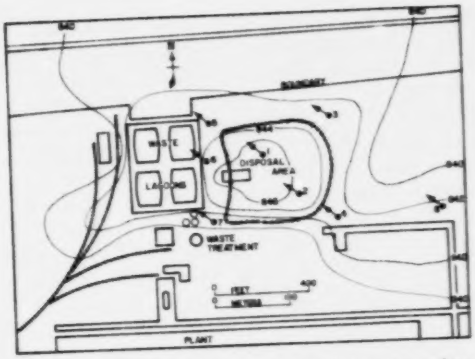
N
BOUNDARY
WASTE
LAGOONS
DISPOSAL AREA
WASTE TREATMENT
FEET
METERS
PLANT

Figure 1. Location of borings at site W. Arrows indicate most probable direction of groundwater movement

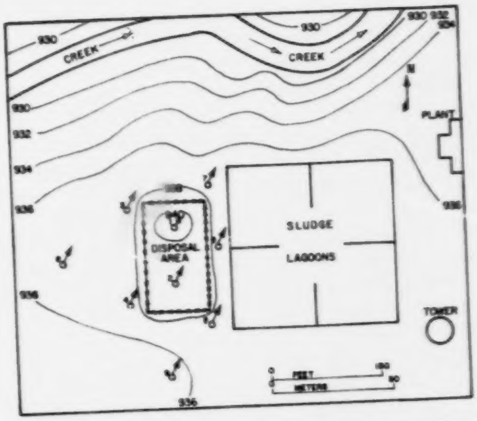
930
CREEK
CREEK
930
930
932
934
N
932
934
936
PLANT
SLUDGE
LAGOONS
DISPOSAL AREA
936
936
TOWER
FEET
METERS
936

Figure 2. Location of borings at site X. Arrows indicate most probable direction of groundwater movement

trimmed to remove any potential cross contamination, and placed in cleaned plastic jars. The jars were packed in ice and shipped to the laboratory for digestion and analysis.

Samples were obtained at 1 to 2 m intervals down each boring to a point below the water table. Particular care was taken to obtain samples immediately below the sludge/soil interface and at the water table. Splits of the soil samples were used for physical testing, chemical analysis, and additional geochemical studies.

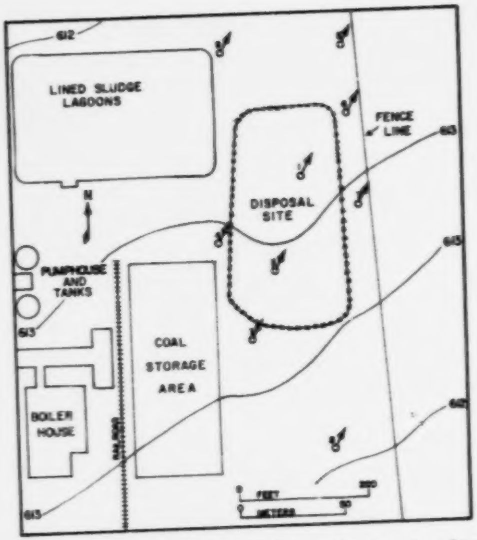
612
LINED SLUDGE
LAGOONS
FENCE
LINE
613
N
DISPOSAL
SITE
613
PUMPHOUSE
AND
TANKS
613
COAL
STORAGE
AREA
BOILER
HOUSE
612
FEET
METERS
613

Figure 3. Location of borings at site Y. Arrows indicate most probable direction of groundwater movement

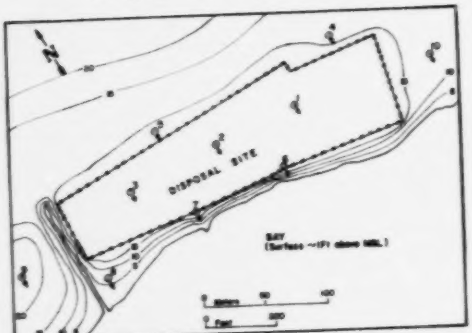
N
DISPOSAL SITE
BAY
Meters
Feet

Figure 4. Location of borings at site Z. Arrows indicate most probable direction of groundwater movement

Analytical Procedures

Approximately 50 g of moist soil was taken from each sample bottle and weighed into a clean, tared, 250-ml fluorocarbon beaker and 60 ml of 8N reagent-grade nitric acid was added. The soil-acid suspension was heated to 95°C for 45 min and stirred every 15 min. After cooling to room temperature, the suspension was filtered through a 0.45-micron membrane filter. The digested soil was washed in the filter three times with 20-ml portions of 8N nitric acid. The filtrate was quantitatively transferred to a 250-ml volumetric flask and brought up to volume with 8 N nitric acid. The acid digests were stored in clean polyethylene bottles. The procedures for the chemical analyses are given in Table 3.

The nitric acid digestion procedure

TABLE 3. TECHNIQUES USED IN THE ANALYSIS OF NITRIC ACID DIGESTS

Constituent	Procedures and/or instrumentation*	Lowest reporting concentration (ppm)
Fe	Determined with Perkin-Elmer Heated Graphite Atomizer Atomic Absorption Unit	0.003
K	Determined with a Spectrametrics Argon Plasma Emission Spectrophotometer Model II	0.05
Mn	Determined with Perkin-Elmer Heated Graphite Atomizer Atomic Absorption Unit	0.001
Na	Determined with Spectrametrics Argon Plasma Emission Spectrophotometer Model II	0.03
B	Same as above	0.02
Be	Determined with a Perkin-Elmer Heated Graphite Atomizer Atomic Absorption Unit	0.005
Cd	Same as above	0.0003
Cr	Same as above	0.003
Cu	Same as above	0.003
Hg	Determined with a Nisseisangyo Zeeman Shift Atomic Absorption Spectrophotometer	0.0002
Ni	Determined with a Perkin-Elmer Heated Graphite Atomizer Atomic Absorption Unit	0.005
Pb	Same as above	0.002
Se	Same as above	0.005
Zn	Same as above	0.014

* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

takes into solution all metals present as carbonates or sulfides or which are adsorbed to clay minerals, iron oxide or insoluble organic materials. Elements in non-clay silicate lattices are not brought into solution.

A separate aliquot of moist soil was taken to determine moisture content of the soils. Moisture contents were used to correct the chemical analyses so that soil acid digests could be expressed in milligrams per kilogram dry weight of soil.

RESULTS AND DISCUSSION

Results of the chemical analyses of the nitric acid digests of the soil samples taken at various depths in the bore holes are given in Tables 4-11 for all four sites. At sites W, X, and Y, borings 1 and 2 are experimental borings through the treated sludge itself (Tables 4, 6, 8). At site Z, the experimental borings are 1, 2, and 3 (Table 10). The remaining borings at each site are control holes which were drilled in the area surrounding the sludge disposal site (Tables 5, 7, 9, 11). The samples from each boring are numbered consecutively down the bore hole - for example, "2C7" represents a sample from boring number 2, chemical testing split (C), seventh sample down the boring from the surface. The elevation above mean sea level, depth below the sludge/soil interface (negative numbers being samples from the treated sludge or cover material), and the height of the sample above or below the watertable are indicated in the tables for each sample. At site W, the major materials disposed were sludges produced in an automobile assembly plant. As can be seen in samples 1C1, 1C2, 2C1, and 2C2 (Table 4), the sludges differ from surrounding soils in having elevated concentrations of all metals determined. The major potential contaminants are boron, chromium, iron, lead, manganese, nickel, and zinc; also, sodium and selenium. Elevated levels of most contaminants were only evident in the samples from the first meter below the sludge/soil interface. No soils samples recovered from borings more than 1 m below the sludge/soil interface had metals levels above that observed in the surrounding uncontaminated soils except in the case of selenium. Selenium levels were higher in deep (greater than 1 m) soils samples in both experimental borings at site W.

The Mann-Whitney U Test was used to detect differences in metal contents between soils collected immediately below the sludge disposal site and those taken from similar elevations outside the disposal area. Significantly elevated levels were found for manganese, sodium, and selenium in samples from the sludge disposal area (Table 12).

The waste disposed at site X was treated electroplating waste. The major potential pollutants contained in this sludge were cadmium, chromium, copper, sodium, and zinc; other constituents present in the sludge at levels in excess of that found in the surrounding soils were boron, mercury, nickel, lead, and selenium. Several metals (iron, potassium, and manganese) were much less prevalent in the treated sludge than in the local soils. No soils samples were taken below 1-m depth under the sludge/soil interface. Significantly elevated levels of iron, sodium, mercury, and nickel, were found in the digest of the

TABLE 4. ANALYSES OF NITRIC ACID DIGESTS OF SOIL SAMPLES FROM EXPERIMENTAL BORINGS AT SITE W

Boring and sample	1C1	1C2	1C3	1C4	1C5	1C6	1C7
Elevation (m)			255.87	254.94	253.73	252.79	250.54
Depth below sludge/soil interface (m)			0.07	1.00	2.21	3.15	5.40
Ht. above water table (m)			2.49	1.56	0.35	-0.59	-2.84
Conc. (mg/kg dry wt.)							
Fe	67709.41	38777.90	30192.42	13621.28	11407.92	13340.41	14054.88
K	211.66	1080.86	768.45	468.35	559.46	580.90	721.00
Mn	1063.65	779.20	893.51	336.76	305.40	328.41	384.19
Na	361.76	601.98	317.91	107.29	111.32	113.14	114.08
B	50.10	30.27	9.40	8.99	9.74	10.80	10.12
Be	0.56	0.46	0.83	0.38	0.36	0.39	0.42
Cd	6.36	4.39	3.33	0.30	0.26	0.89	0.13
Cr	367.12	195.69	21.41	9.94	9.44	9.68	10.37
Cu	40.71	41.73	29.63	16.51	13.25	15.70	15.61
Hg	0.09	0.08	0.02	0.01	0.01	0.01	0.01
Ni	95.88	68.56	30.28	23.31	20.50	19.92	20.98
Pb	66.90	17.17	14.06	4.62	4.55	6.71	7.26
Se	0.80	0.86	0.49	0.77	0.82	0.73	0.86
Zn	1630.64	1184.26	72.24	54.11	47.01	55.30	44.63

(continued)

TABLE 4. (Concluded)

Boring and sample	2C1	2C2	2C3	2C4	2C5	2C6	2C7
Elevation (m)			256.51	255.60	254.38	253.45	251.40
Depth below sludge/soil interface (m)			0.08	0.99	2.21	3.14	5.55
Ht. above water table (m)			4.31	3.22	2.00	1.07	-1.34
Conc. (mg/kg dry wt.)							
Fe	26272.88	17532.36	15162.99	20867.45	13576.87	8662.46	9075.01
K	266.41	1330.04	483.10	773.94	735.41	435.69	339.28
Mn	626.08	479.58	1084.29	439.32	319.58	239.66	293.43
Na	330.25	1439.87	357.92	206.91	180.08	102.61	119.60
B	36.82	11.88	5.31	10.56	11.02	6.96	7.14
Be	0.44	0.45	0.54	0.67	0.37	0.29	0.22
Cd	2.84	2.25	1.55	2.43	1.73	1.16	1.13
Cr	98.66	30.99	12.92	15.99	11.65	9.31	12.70
Cu	16.82	20.35	11.11	24.30	17.06	15.34	11.54
Hg	0.02	0.07	0.03	0.02	0.02	0.01	0.00
Ni	54.13	27.40	13.92	32.22	24.50	17.95	13.01
Pb	10.99	18.09	14.06	9.64	7.50	6.73	5.94
Se	1.12	0.84	0.46	0.67	1.77	0.18	0.21
Zn	1048.46	229.73	48.22	79.24	60.06	52.65	38.85

TABLE 5. ANALYSES OF NITRIC ACID DIGESTS OF SOIL SAMPLES FROM CONTROL BORINGS AT SITE W

Boring and sample	3C1	3C2	3C3	3C4	3C5	3C6	4C6	5C1
Elevation (m)	256.84	255.93	254.71	253.81	251.20	249.37	250.75	256.68
Ht. above water table (m)	6.16	5.25	4.03	3.13	0.52	-1.31	-1.02	5.63
Conc. (mg/kg dry wt.)								
Fe	17024.76	16985.11	13627.81	12422.47	14003.01	15313.91	8674.08	14464.37
K	634.06	692.73	546.98	645.28	687.69	897.67	380.32	618.49
Mn	445.30	403.24	378.62	291.06	344.21	420.64	258.93	364.36
Na	110.71	100.59	111.59	120.52	111.70	124.55	100.51	141.87
B	10.23	9.68	10.34	10.75	10.00	10.15	6.39	12.80
Be	0.23	0.49	0.34	0.29	0.31	0.32	0.08	0.32
Cd	2.18	2.04	1.79	1.59	1.43	1.70	1.08	2.01
Cr	40.15	20.56	17.17	17.68	16.31	17.68	10.02	17.68
Cu	27.59	18.12	14.27	13.16	12.42	14.21	8.51	20.77
Hg	0.03	0.01	0.01	0.04	0.02	0.01	0.01	0.02
Ni	21.17	24.24	19.34	17.93	15.20	18.49	10.27	18.68
Pb	11.74	10.44	10.98	7.42	6.67	7.38	5.34	21.33
Se	0.25	0.24	0.25	0.23	0.23	0.23	0.23	0.23
Zn	126.64	57.32	53.42	50.16	43.68	90.41	35.59	82.43

continued

TABLE 5. (Concluded)

Boring and sample	5C6	6C1	6C5	7C1	7C2	7C3	7C4	7C5	8C6
Elevation (m)	250.60	257.07	252.68	255.97	255.21	253.99	253.07	251.55	250.55
Ht. above water table (m)	-0.45	2.33	-2.06	2.82	2.06	0.84	-0.07	-1.60	1.33
Conc. (mg/kg dry wt.)									
Fe	12693.60	18631.07	9209.18	13957.05	23965.56	13565.70	8430.77	9744.03	13705.00
K	584.46	667.09	432.44	377.54	608.69	575.11	373.00	263.86	621.41
Mn	393.56	329.14	299.06	358.99	522.73	390.73	235.49	199.62	301.32
Na	126.09	185.36	143.85	89.13	79.02	111.77	121.34	94.87	109.83
B	11.25	28.58	10.61	6.76	11.98	13.18	11.14	7.64	10.70
Be	0.23	0.77	0.27	0.36	0.73	0.29	0.19	0.06	0.22
Cd	1.40	3.00	1.18	1.50	2.55	1.73	1.20	1.10	1.36
Cr	14.54	23.82	11.99	12.17	19.67	14.86	12.81	26.04	14.22
Cu	12.01	120.67	9.47	8.21	21.71	13.66	45.21	10.48	43.37
Hg	0.01	0.07	0.01	0.02	0.02	0.01	0.01	0.01	0.01
Ni	15.80	23.98	12.75	9.28	30.61	19.06	18.29	8.21	14.97
Pb	6.82	22.20	14.03	6.73	10.42	8.60	8.99	3.96	6.57
Se	0.14	0.16	0.18	0.08	0.25	0.47	0.49	0.68	0.33
Zn	36.98	158.32	35.70	38.51	72.59	53.02	83.77	29.15	43.37

TABLE 6. ANALYSES OF NITRIC ACID DIGESTS OF SOIL SAMPLES FROM EXPERIMENTAL BORINGS AT SITE X

Boring and sample	1C1	1C2	2C1	2C2
Elevation (m)		285.32		285.33
Depth below sludge/soil interface (m)		0.09		0.07
Ht. above water table (m)		2.65		2.40
Conc. (mg/kg dry wt.)				
Fe	3494.40	22579.62	4579.29	23090.18
K	50.74	837.14	125.63	950.77
Mn	90.47	498.00	128.66	600.54
Na	952.58	664.89	1610.86	883.97
B	30.73	13.12	40.12	15.46
Be	0.69	0.49	0.90	0.70
Cd	109.14	2.44	102.32	2.76
Cr	1493.45	14.14	1783.04	18.08
Cu	1531.79	28.20	1772.95	26.56
Hg	0.26	0.04	0.17	0.03
Ni	42.65	26.28	56.28	21.36
Pb	18.19	11.60	21.28	11.89
Se	0.45	0.22	2.12	0.27
Zn	413.58	67.47	481.23	84.36

TABLE 7. ANALYSES OF NITRIC ACID DIGESTS OF SOIL SAMPLES FROM CONTROL BORINGS AT SITE X

Boring and sample	3C1	3C2	3C3	4C1	5C1	5C2
Elevation (m)	285.35	284.45	282.19	285.45	285.83	284.91
Ht. above water table (m)	1.97	1.07	-1.19	2.08	2.45	1.53
Conc. (mg/kg dry wt.)						
Fe	22852.51	35987.73	11.32	22466.78	17202.49	18357.78
K	912.40	719.75	565.90	572.06	867.44	637.19
Mn	619.06	673.07	238.08	599.77	933.33	453.61
Na	85.27	44.98	154.56	95.01	25.62	151.60
B	17.14	17.31	21.19	9.06	8.15	27.36
Be	0.78	0.98	0.36	0.46	0.41	0.34
Cd	3.34	3.14	1.48	7.99	2.10	1.92
Cr	42.42	36.28	12.78	76.85	17.52	15.10
Cu	25.84	32.17	12.09	93.43	38.25	41.10
Hg	0.02	0.03	0.02	0.03	0.02	0.03
Ni	24.43	78.72	16.64	20.64	14.96	24.10
Pb	12.79	12.73	8.72	13.86	12.81	11.84
Se	1.02	0.28	0.45	1.19	1.17	0.99
Zn	72.48	30.30	45.87	77.89	59.02	98.54

(continued)

TABLE 7. (Concluded)

Boring and sample	6C1	6C2	7C1	7C2	8C1	9C1
Elevation (m)	285.56	284.66	285.52	284.59	285.55	285.19
Ht. above water table (m)	2.18	1.28	2.22	1.29	2.19	2.11
Conc. (mg/kg dry wt.)						
Fe	14961.01	40577.16	13444.79	23916.70	20850.39	16176.78
K	473.20	907.77	388.71	347.03	562.01	385.75
Mn	578.27	814.27	364.90	487.68	754.38	723.48
Na	59.68	47.20	55.79	34.70	37.91	105.77
B	7.92	15.16	4.52	7.87	7.77	5.93
Be	0.36	1.05	0.36	0.59	0.46	0.44
Cd	1.50	3.33	BDI	0.03	0.44	5.44
Cr	10.46	19.74	7.79	17.58	25.45	95.95
Cu	25.97	34.86	35.21	20.54	22.08	80.08
Hg	0.02	0.02	0.01	0.03	0.02	0.02
Ni	14.83	46.16	10.75	19.27	16.35	13.73
Pb	10.09	18.16	10.06	12.19	13.27	11.55
Se	1.14	1.04	0.48	BDL	0.52	0.59
Zn	61.10	125.27	45.18	72.22	56.58	61.24

BDL = Below detection limits.

TABLE 8. ANALYSES OF NITRIC ACID DIGESTS OF SOIL SAMPLES FROM EXPERIMENTAL BORINGS AT SITE Y

Boring and sample	1C1	1C2	1C3	2C1	2C2	2C3	2C4	2C5	2C6
Elevation (m)	186.55	185.67	184.91	186.85	185.92	185.19	183.79	181.21	179.21
Depth below sludge/soil interface (m)**									
Ht. above water table (m)	1.35	0.47	-0.29	9.68	8.75	8.02	6.62	4.04	2.04
Conc. (mg/kg dry wt.)									
Fe	15877.04	9403.42	20457.00	24215.85	21591.43	21366.44	22986.16	19866.21	17554.88
K	331.73	110.63	911.11	1114.84	369.45	972.08	961.24	562.88	566.45
Mn	650.13	134.57	299.09	494.34	302.25	255.02	327.63	270.37	176.54
Na	1800.58	262.74	97.13	2147.44	369.45	97.21	109.50	71.74	75.53
B	9.05	3.60	10.66	10.51	6.52	10.78	10.62	8.02	7.55
Be	0.46	0.18	0.41	0.71	0.33	0.27	0.27	0.42	0.45
Cd	0.03	BDL	0.04	0.26	BDL	0.19	0.49	BDL	BDL
Cr	45.28	11.11	15.51	13.66	11.85	14.48	10.91	5.99	5.81
Cu	17.12	9.50	20.89	18.09	13.63	19.34	21.56	20.20	18.17
Hg	0.02	0.02	BDL	0.02	0.02	0.02	0.01	0.01	0.01
Ni	36.68	9.36	28.58	24.08	20.68	25.26	25.62	20.69	20.06
Pb	70.96	5.43	8.60	12.79	4.80	7.70	8.36	8.83	9.18
Se	0.67	BDL	BDL	0.59	BDL	BDL	BDL	BDL	BDL
Zn	353.02	55.96	60.60	63.24	65.54	65.16	69.54	78.58	68.08

BDL = Below detection limits.

** = Sludge removed at this site.

TABLE 9. ANALYSES OF NITRIC ACID DIGESTS OF SOIL SAMPLES FROM CONTROL BORINGS AT SITE Y

Boring and sample	3C1	3C2	3C3	3C4	3C5	4C1	4C2	4C3
Elevation (m)	186.94	186.02	185.26	184.13	181.43	186.92	185.99	185.23
Ht. above water table (m)	9.82	8.90	8.14	7.01	4.31	9.53	8.60	7.84
Conc. (mg/kg dry wt.)								
Fe	24269.17	36164.67	27242.40	20723.46	17832.90	20436.30	25864.15	19465.27
K	763.01	562.86	1375.61	731.66	422.36	519.28	318.48	489.08
Mn	561.66	530.03	210.36	225.82	335.99	409.55	283.75	346.25
Na	86.41	43.43	115.98	93.04	90.10	229.49	153.45	89.99
B	11.49	13.03	14.20	10.40	7.48	7.87	8.59	9.39
Be	0.65	1.20	0.87	0.52	0.10	0.59	0.82	0.44
Cd	0.28	1.36	0.73	0.22	1.48	1.76	2.08	1.84
Cr	12.09	14.76	17.40	10.19	7.47	11.47	13.70	10.37
Cu	21.79	30.05	26.25	22.16	21.92	17.14	18.10	22.16
Hg	0.02	0.02	0.08	0.20	0.12	0.02	0.21	0.02
Ni	31.12	34.52	34.39	23.98	19.46	24.65	25.31	27.12
Pb	10.11	9.75	8.99	8.46	8.45	9.21	7.72	8.80
Se	0.10	BDL	BDL	BDL	BDL	0.24	BDL	BDL
Zn	65.27	80.57	68.78	74.35	60.72	55.86	61.96	63.09

(continued)

TABLE 9. (Continued)

Boring and sample	4C4	4C5	4C6	4C7	5C1	5C2	5C3	5C4
Elevation (m)	183.87	181.43	179.23	177.16	186.64	185.73	184.97	183.58
Ht. above water table (m)	6.48	4.04	1.84	-0.23	9.74	8.83	8.07	6.68
Conc. (mg/kg dry wt.)								
Fe	20435.79	17808.00	17740.80	19266.13	19305.95	13473.95	13749.88	26527.58
K	937.01	926.38	858.58	628.68	807.70	294.92	344.26	700.06
Mn	280.19	325.56	242.85	298.27	477.90	481.46	709.88	445.77
Na	103.52	98.03	96.77	96.33	111.67	63.13	81.48	72.65
B	12.05	11.42	12.33	9.72	12.49	5.54	6.19	11.23
Be	0.53	0.48	0.37	0.30	0.62	0.47	0.55	0.59
Cd	1.99	1.65	1.80	1.54	2.00	1.32	1.27	2.57
Cr	13.21	11.87	8.66	8.70	15.62	9.42	0.97	10.79
Cu	23.88	25.60	19.12	18.13	54.95	7.28	11.06	32.65
Hg	0.02	0.01	BDL	0.02	0.05	0.10	0.06	0.02
Ni	35.72	25.03	25.07	22.08	23.88	12.18	13.68	37.02
Pb	10.71	7.20	9.49	8.45	18.93	5.65	7.13	12.11
Se	BDL	BDL	BDL	BDL	0.18	BDL	BDL	BDL
Zn	63.90	52.61	74.28	77.49	149.53	46.83	46.75	132.09

(continued)

TABLE 9. (Continued)

Boring and sample	5C5	5C6	5C7	6C6	7C5	8C1	8C2	8C3
Elevation (m)	181.14	179.01	176.86	179.09	177.06	186.55	185.62	183.45
Ht. above water table (m)	4.24	2.11	-0.04	2.14	-2.01	9.01	8.08	5.91
Conc. (mg/kg dry wt.)								
Fe	24518.92	16899.77	17360.29	13259.11	21145.56	22177.23	10968.34	14555.71
K	633.10	687.07	434.01	272.60	503.15	439.74	293.14	276.47
Mn	374.64	228.08	309.08	128.86	268.04	521.54	179.51	347.82
Na	67.70	44.33	114.32	53.78	68.91	134.20	119.39	33.87
B	8.69	7.76	14.82	3.18	8.18	3.24	2.84	3.91
Be	0.55	0.46	0.23	0.25	0.35	0.36	0.30	0.38
Cd	1.98	1.52	2.94	1.46	5.28	1.37	1.73	1.84
Cr	9.42	0.02	9.88	6.78	10.52	8.96	7.50	5.83
Cu	25.58	18.89	26.21	16.47	22.75	9.33	9.61	17.58
Hg	0.18	0.42	0.22	0.52	0.02	0.03	0.02	0.01
Ni	31.86	22.74	30.09	18.39	31.08	15.35	13.33	17.05
Pb	10.98	9.23	8.74	6.49	9.44	9.52	5.82	6.41
Se	BDL	BDL	BDL	BDL	0.15	0.55	BDL	BDL
Zn	85.63	63.72	134.44	59.34	103.70	52.87	55.47	63.67

(continued)

TABLE 9. (Concluded)

Boring and sample	8C4	8C5	8C6	9C1	9C2	9C3	9C4
Elevation (m)	181.04	178.91	177.06	186.66	185.74	185.00	183.63
Ht. above water table (m)	3.05	1.37	-0.48	9.82	8.90	8.61	6.79
Conc. (mg/kg dry wt.)							
Fe	17877.82	22857.84	17456.36	21687.46	11310.70	21324.99	20166.66
K	752.75	48.74	468.10	842.40	225.24	1028.17	1100.99
Mn	262.46	343.75	84.77	436.38	87.89	471.19	394.55
Na	64.92	53.40	45.59	673.03	86.78	96.15	109.01
B	9.24	10.68	5.87	9.23	3.62	11.04	11.12
Be	1.13	0.43	0.37	0.72	0.36	0.64	2.77
Cd	2.29	1.90	1.38	1.78	0.60	1.84	2.05
Cr	10.20	10.62	6.70	14.20	9.79	14.32	12.69
Cu	21.17	28.95	20.12	18.19	7.98	19.32	19.62
Hg	0.02	0.02	0.02	0.03	0.02	0.02	0.01
Ni	28.35	34.78	23.83	25.84	9.97	26.59	28.05
Pb	9.41	11.24	7.78	8.96	2.85	7.62	8.72
Se	0.12	BDL	BDL	BDL	BDL	0.19	0.05
Zn	68.92	87.26	80.67	62.96	39.44	59.64	66.44

BDL = Below detection limits.

TABLE 10. ANALYSES OF NITRIC ACID DIGESTS OF SOIL SAMPLES FROM EXPERIMENTAL BORINGS AT SITE Z

Boring and sample	1C1	1C2	1C3	1C4	1C5	1C6	1C7	1C8	2C1	2C2
Elevation (m)	5.61	4.09	2.46	1.54	0.32	-0.59	-2.12	-3.64	5.17	3.64
Depth below sludge/soil interface (m)	-3.05	-1.53	0.10	1.02	2.24	3.15	4.68	6.20	-3.05	-1.52
Ht. above water table (m)	5.15	3.63	2.00	1.08	-0.14	-1.05	-2.58	-4.10	4.03	2.50
Conc. (mg/kg dry wt.)										
Fe	8230.47	15804.15	24469.34	24149.29	18865.61	16047.70	13435.52	13105.36	7559.94	15823.24
Mn	60.80	267.84	614.57	291.68	283.44	1381.88	78.39	23.08	89.77	292.27
Na	163.28	1007.77	713.23	1138.33	987.39	755.13	597.53	241.28	162.78	448.49
B	1.93	5.00	6.96	7.60	6.45	6.75	4.22	4.24	2.11	3.81
Be	0.48	1.30	1.91	1.92	1.66	1.49	1.37	0.95	0.39	0.99
Cd	1.05	2.45	2.84	2.89	2.39	2.42	1.74	1.73	1.08	1.99
Cr	12.69	742.93	24.12	22.38	18.80	17.41	14.52	9.22	20.58	212.58
Cu	4.98	139.57	15.17	16.76	14.27	12.93	8.01	7.95	8.02	48.68
Hg	0.09	10.97	0.01	BDL	BDL	BDL	0.01	BDL	0.24	2.29
Ni	4.96	21.74	25.40	25.27	20.91	30.47	14.30	11.87	5.60	16.81
Pb	92.43	4751.46	36.18	29.12	29.42	33.12	14.28	15.93	15.73	2328.08
Se	0.13	0.54	0.86	0.66	0.30	0.87	0.52	0.34	0.50	0.78
Zn	19.80	442.28	54.04	68.16	57.04	51.69	38.96	27.28	33.20	149.14

continued

TABLE 10. (Concluded)

Boring and sample	2C3	2C4	2C5	2C6	3C1	3C2	3C3	3C4	3C5	3C6
Elevation (m)	2.01	1.10	-0.12	-1.04	5.14	3.61	1.98	1.07	-0.15	-1.07
Depth below sludge/soil interface (m)	0.11	1.02	2.24	3.16	-3.05	-1.52	0.11	1.02	2.24	3.16
Ht. above water table (m)	0.87	-0.04	-1.26	-2.18	6.10	4.57	2.94	2.03	0.18	-0.11
Conc. (mg/kg dry wt.)										
Fe	21350.54	20433.11	21178.35	19583.95	10935.74	18975.67	14570.30	20138.28	18907.56	15161.72
Mn	364.20	211.96	195.55	76.26	337.92	266.86	103.07	149.16	228.34	120.55
Na	860.78	966.28	748.00	681.84	383.65	2554.94	1240.95	1232.54	1033.98	743.47
B	5.51	6.10	5.98	4.94	3.31	10.56	3.38	5.50	5.22	3.69
Be	1.13	1.17	1.06	1.25	0.75	1.14	1.00	1.08	1.05	1.06
Cd	2.42	2.22	2.25	1.97	1.50	3.69	1.59	2.21	2.24	1.78
Cr	20.12	20.84	19.67	19.79	75.68	1926.84	14.70	16.90	16.19	13.18
Cu	16.71	13.94	13.70	10.33	23.57	200.16	11.89	13.89	12.88	0.88
Hg	0.01	BDL	BDL	0.01	0.73	5.13	0.02	CI	CI	BDL
Ni	23.94	21.75	20.44	18.58	13.43	35.68	15.84	19.65	18.89	17.24
Pb	51.44	26.02	25.01	20.98	537.78	2806.02	18.98	21.86	26.90	19.13
Se	0.40	0.64	0.86	0.84	0.75	1.16	0.37	0.52	0.48	0.55
Zn	63.45	59.94	53.69	48.76	82.44	975.22	45.27	49.95	50.49	34.96

TABLE 11. ANALYSES OF NITRIC ACID DIGESTS OF SOIL SAMPLES FROM CONTROL BORINGS AT SITE Z

Boring and sample	4C1	4C2	4C3	4C4	4C5	5C1	5C2	5C3
Elevation (m)	1.99	1.03	-0.14	-1.05	-2.58	2.15	1.24	0.02
Ht. above water table (m)	0.65	-0.24	-1.48	-2.39	-3.92	0.99	0.08	-1.14
Conc. (mg/kg dry wt.)								
Fe	20880.57	18826.87	16938.52	13209.13	16241.00	20992.32	18581.89	20227.31
Mn	576.07	182.58	136.22	131.17	272.77	491.73	413.56	288.16
Na	860.39	938.50	689.19	720.58	536.58	679.61	788.06	829.41
B	5.40	5.18	4.80	3.43	3.33	4.02	4.50	5.09
Be	1.17	1.10	0.85	1.16	0.88	1.06	1.08	1.15
Cd	2.47	2.08	1.88	1.57	1.88	2.40	2.23	2.26
Cr	17.18	14.98	15.08	12.32	11.87	16.61	15.37	19.79
Cu	13.89	12.68	9.95	7.01	9.87	15.72	14.01	14.96
Hg	CI	CI	CI	BDL	BDL	CI	BDL	BDL
Ni	23.28	18.43	14.41	17.20	18.56	23.85	22.95	21.69
Pb	34.63	23.32	22.63	19.54	23.64	31.58	28.82	28.77
Se	1.27	1.07	0.96	0.93	0.94	0.56	0.70	0.70
Zn	54.42	46.81	38.52	33.41	44.66	55.19	52.58	58.53

(continued)

TABLE 11. (Continued)

Boring and sample	5C4	5C5	6C1	6C2	6C3	6C4	6C5	6C6
Elevation (m)	-0.90	-2.42	2.06	1.14	-0.08	-0.99	-2.52	-4.04
Ht. above water table (m)	-2.06	-3.58	0.93	0.01	-1.21	-2.11	-3.65	-5.17
Conc. (mg/kg dry wt.)								
Fe	15093.02	12363.93	22073.16	20138.13	23213.19	21385.59	21547.15	26061.62
Mn	87.74	112.23	585.03	377.34	223.12	192.19	29.53	1040.64
Na	621.27	408.62	694.42	896.80	762.98	713.76	345.80	301.34
B	2.75	2.54	4.50	5.26	6.62	4.54	5.11	6.03
Be	0.55	0.79	1.07	1.20	1.02	1.14	1.04	1.15
Cd	1.60	1.46	2.43	2.38	2.78	2.54	2.53	3.13
Cr	15.47	11.25	18.59	20.07	27.11	20.51	20.10	19.84
Cu	7.73	9.91	14.84	15.15	11.43	10.38	10.25	13.57
Hg	BDL	BDL	BDL	BDL	0.00	BDL	BDL	0.01
Ni	9.11	14.45	24.40	23.79	17.08	16.13	16.40	21.16
Pb	16.28	14.16	33.84	36.84	24.43	19.81	15.86	37.96
Se	0.71	0.45	0.59	0.56	0.59	0.56	0.68	0.74
Zn	34.38	31.72	60.82	61.80	50.90	46.81	54.54	54.00

(continued)

TABLE 11. (Concluded)

Boring and sample	7C1	7C2	7C3	7C4	7C5	8C5	9C5	10C2
Elevation (m)	1.98	1.07	-0.15	-1.06	-2.59	-2.81	-2.55	1.11
Ht. above water table (m)	0.96	0.05	-1.17	-2.08	-3.61	1.03	6.67	2.71
Conc. (mg/kg dry wt.)								
Fe	26560.80	20633.29	17637.50	19919.02	21003.51	18402.23	22972.47	27836.84
Mn	253.22	176.46	269.64	182.28	379.50	497.11	222.27	283.19
Na	1182.38	988.23	626.64	606.46	404.74	832.02	544.08	1026.48
B	6.87	4.99	4.61	5.31	4.95	2.88	4.82	6.31
Be	1.48	1.04	0.83	2.19	1.00	0.85	1.00	1.44
Cd	3.15	2.60	2.25	2.59	2.77	2.54	3.14	3.56
Cr	29.83	20.30	16.22	18.61	19.14	13.28	14.35	19.55
Cu	15.23	12.94	9.33	10.94	12.98	8.16	8.99	11.50
Hg	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Ni	22.45	18.17	14.40	18.21	20.98	12.63	15.05	16.51
Pb	26.23	22.31	24.46	25.56	20.06	29.61	32.32	27.11
Se	0.55	0.83	0.80	0.84	0.84	0.79	0.70	0.68
Zn	70.23	53.82	40.26	47.37	45.41	35.39	38.39	53.72

BDL = Below detection limits.

CI = Chemical interference.

TABLE 12. RESULTS OF MANN-WHITNEY U TEST OF NITRIC ACID DIGESTS OF SOIL SAMPLES DIRECTLY UNDER THE DISPOSAL SITES AND AT COMPARABLE ELEVATIONS OUTSIDE THE DISPOSAL SITES

Parameter Measured	Site W	Site X	Site Y	Site Z
Fe	NS	S	NS	NS
K	NS	NS	NS	NS
Mn	S	NS	NS	NS
Na	S	S	S	NS
B	NS	NS	NS	NS
Be	NS	NS	NS	NS
Cd	NS	NS	NS	NS
Cr	NS	NS	NS	NS
Cu	NS	NS	NS	NS
Hg	NS	S	NS	NA
Ni	NS	S	NS	NS
Pb	NS	NS	NS	NS
Se	S	NS	NA	NS
Zn	NS	NS	NS	NS

S = Metal level significantly larger under the disposal site at a 0.10 level of significance.

NS = Metal level not significantly larger under the disposal site at a 0.10 level of significance.

NA = Too few samples to test statistically.

soil from less than 1 m under the treated sludge when compared to surrounding soils at similar elevations (Table 12). Iron is not a prominent constituent in the treated electroplating sludge, therefore, the elevated levels of iron under the waste disposal site are probably due to chance variation.

The treated automobile assembly plant waste (largely paint and putty) deposited at site Y had been in place for approximately 9 months before the material was removed to a landfill and the area was regraded. Major potential pollutants from this treated sludge were chromium, iron, lead, manganese, sodium, and zinc. Only sodium was found at significantly elevated levels in soils samples taken near the surface from which the treated sludge had been removed (Table 12). However, high levels of chromium, lead, and zinc were found in samples from the upper level of one of the experimental holes (1C1, Table 8). The sodium levels in the soils samples taken approximately 1 m deeper in both experimental holes (samples 1C2 and 2C2) were still slightly above the range of sodium levels in the surrounding soils. Sodium levels for soils samples taken from greater depths below the sludge/soil interface were within the range of sodium levels in the surrounding soil.

Site Z contains treated refinery sludge which had been covered with 0.5 m of clay. Three experimental borings were drilled through the cover material and the treated sludge to the watertable (Table 10). The major pollutants at this site are chromium, copper, mercury, lead, and zinc. Slightly elevated levels of boron, cadmium, and sodium were also detected in experimental boring No. 3. The top samples in each of the experimental borings (1C1, 2C1, and 3C1) reflect the composition of the covering clay layer and bear little relation to either the treated sludge sample or the underlying soils. The second sample from each boring (sample 1C2, 2C2, and 3C2) contained a large portion of the treated sludge as can be noted by the high concentrations of the potential pollutants. However, the levels of all potential pollutants in the third sample down each experimental hole (samples 1C3, 2C3, and 3C3) are all within the range of these constituents in the surrounding soils even though these samples were taken only 10 to 12 cm below the sludge/soil interface. In only one case (lead in sample 2C3) is any sample from an experimental boring above the range observed in surrounding soils. No significant loss of pollutants to the soil under the treated sludge disposal area was detected when samples from below the disposal pit were compared to surrounding soils at similar elevations (Table 12).

The soils at all four sites have concentrations for the constituents tested which fall within the typical concentration ranges for soils in a natural state in the eastern United States (Table 13). All of the soils have concentrations near to or below the average for such soils. Even in the cases where significant increases in the constituents under the treated sludge were found, these elevated levels were always well within typical ranges for eastern soils. For instance, sodium, which was found at levels of 357, 883, and 2147 mg/kg dry weight of soil under the sludges at sites W, X, and Y, respectively, has an average concentration in eastern soils of 2600 mg/kg—higher than any "contaminated" sample found.

TABLE 13. CONCENTRATIONS OF SELECTED CONSTITUENTS IN SOILS IN THE EASTERN UNITED STATES

Constituent	Concentration*	
	Average	Range
Fe	15,000**	100 - >100,000
K	7400	50 - 370,000
Mn	290	<2 - 7,000
Na	2600	<200 - 15,000
B	32	<10 - 150
Be	0.6	<1 - 7
Cd	<1	<1 - 4
Cr	36	1 - 100
Cu	13	3 - 100
Hg	0.096	.01 - 3.4
Ni	13	<3 - 700
Pb	14	<7 - 300
Se	0.39	<.1 - 1.4
Zn	36	<5 - 400

* Concentrations are in milligrams per kilogram dry wt of soil.

** Soil analyses are for Eastern U. S. soils as given by Connor and Shacklette.[4]

Three of these significantly contaminated soils samples taken at the sludge/soil interface - selenium at site W, iron and nickel at site Y - had maximum value less than twice the average soil concentration and well within typical ranges. In the "worst case" noted, that of manganese contamination, at site W, the highest contaminant level was less than four times the average, and was still well within typical ranges for manganese in eastern soils. Even in the cases where significant contamination was found, appreciable degradation of the soil below that of typical eastern soil could not be demonstrated.

CONCLUSIONS

The loss of contaminants from disposal areas containing treated industrial wastes to the soils below the disposal area has been examined. Analyses of nitric acid digest of soils samples taken at various depths under and immediately surrounding four disposal areas has shown only a minor gain of potential pollutants by underlying soils. Although elevated levels of a limited number of constituents which could be related to the presence of the treated wastes were detected in the first meter of soil under the sludge/soil interface, in no case were these levels higher than the typical range for these elements in eastern United States soils. Attenuation of pollutants from the leaching medium by the underlying soil does not seem to be a major factor in maintaining high quality groundwater under the studied sites.

At one site (site Y) the treated sludge had been removed after being in place for less than 9 months and the site was subsequently regraded. The presence of the disposal area was still evident in significantly higher sodium levels in all soils samples. Some of the individual soils samples also had metals concentrations outside the range of concentrations found in surrounding soils. In no case was the residual amount of any measured metal beyond the range encountered in natural soils for the eastern United States.

The only site in which no significant effect of the treated sludge was measured (site Z) was unique in that it had been covered with 0.5 m of clay. Even though it has the highest mean annual rainfall for the sites studied, the clay cover may have been effective in precluding percolation through the treated sludge into the soil below since no contamination of the soil was evident.

The results of this study corroborate and correlate well with our previous studies at these four sites on the physical properties of the underlying soils and on the chemistry of groundwater samples under and down dip from the disposal area.[5] No effect of the disposal areas on the physical properties of underlying soils samples, when compared to surrounding soils, was found. None of the toxic constituents (with the exception of phenols at site Z) predicted to be pollution problems on the basis of their presence in the treated sludges was found at significantly elevated levels in the groundwater. No unusual accumulations of toxic elements in the soil under the disposal areas were found.

The absence of changes in the physical properties and the lack of major changes in chemical composition in the soils underlying the treated waste disposal areas, and the absence of evidence of major pollutants in the groundwater under and down dip from the waste disposal area may be attributed to the short time available for the transport of the material out of the treated sludges or to the efficacy of the treatment process. The treated waste had been in place for only 3 to 4 years at the sites studied. Further work is necessary in order to determine the long-term efficacy of the treatment and disposal operations.

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LEACHATE FROM MUNICIPAL AND INDUSTRIAL WASTE LANDFILL SIMULATERS

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ABSTRACT

In late 1974, a simulated landfill study was initiated to study landfill behavior under controlled conditions. A total of 19 test cells was constructed to study different infiltration rates, pH buffering compounds, prewetting the wastes and co-disposing refuse with sewage sludge and various industrial wastes. Each cell received approximately 3.2 metric tons of municipal refuse. Twelve received municipal refuse plus small quantities of industrial wastes and other materials. Water additions were made on all cells on a preset schedule to approximate Midwest U.S. infiltration rates. Quality and quantity data were collected on leachate and gas produced.

This paper addresses data collected from leachate and gas analysis for the cells which contained municipal refuse plus industrial wastes. Data encompass the period from November, 1974 to August, 1978. Mass releases of leachate constituents were plotted and studied. Gas quantities and qualities were studied also. Data continue to be collected and analyzed on this project.

INTRODUCTION

Under the Resource Conservation and Recovery Act of 1976 (RCRA), an inventory of all solid waste disposal sites is to be made across the nation. In addition, all sites identified by the inventory must be classified as either a "sanitary landfill" or an "open dump". Sites found to be in compliance with the Classification Criteria for Solid Waste Disposal Sites(1) (and thus posing no significant threat to human health or the environment) will be classified as sanitary landfills. Sites found to be in non-compliance with the criteria will be classified as open dumps. Open dumps must be either closed immediately or upgraded as necessary to mitigate the hazard identified by the inventory. The closure and upgrading procedures required will depend in large measure on the degree and status of the hazard. That is, if the hazard is large and yet to be fully exercised expensive confinement and/or waste removal procedures may be dictated. If the hazard is large but most of the damage is already done, money would be better directed toward clean-up than confinement and/or removal. Lastly, if the hazard is small, the site may be simply closed and funds used elsewhere.

A framework to assist in these decisions needs to be established. From numerous previous studies, data for such a framework has been generated on the decomposition processes in landfills and the release of contaminants from landfills into the environment. However, many of these efforts have had relatively short-lived monitoring terms. In addition, the variability and unknowns of initial conditions among such studies have made comparisons of data and compilation of large data bases difficult and often impossible.

This project was motivated by the need for such a data base. The broad objective of the program was to study solid waste decomposition and contaminant release at various types of landfills.

Specific objectives were to determine:

1. The effect of different water infiltrations on solid waste decomposition.
2. The effect of sewage sludge additions on solid waste decomposition.
3. The effect of pH buffer addition on solid waste decomposition.
4. The effect of six selected industrial sludge additions on solid waste decomposition.
5. The effect of initial water addition on solid waste decomposition.
6. The survivability of poliovirus in landfills.
7. The effect of different air and soil ambient temperatures on solid waste decomposition.
8. The ability to duplicate monitoring data from two test cells constructed and operated under similar conditions.

TEST CELL CONSTRUCTION

The experimental test facility for this project is located at the U.S. Environmental Protection Agency's Center Hill Laboratory in Cincinnati, Ohio. A total of 19 test cells were constructed for this effort in November, 1974 and April, 1975. Fifteen of these are located outdoors and below the ground surface. These exterior test cells are arranged in a horseshoe alignment as shown in Figure 1. The remaining 4 cells are located inside the high bay area of the Center Hill Laboratory and are above ground resting on the concrete slab.

Individual test cells consist of steel tubes 1.83 m in diameter, 3.66m high and 4.76 mm thick. Steel sidewalls were coated with coal tar epoxy as a moisture seal. The outside test cells were placed on concrete slabs in a excavated area. Soil was then backfilled around the sidewalls to within 0.3 m of the top of the cell. Several layers of fiberglass cloth were placed inside at the base of these cells and extended 0.3 m up the sidewall to provide a watertight and gas tight seal. The interior test cells were placed atop steel bases welded into place.

Provisions for leachate drainage were installed for all cells. Exterior cells had a small depression in the concrete slab and connective piping to a leachate collection well. This well serves as a central leachate collection point for all exterior cells. It is also used as a groundwater drawdown to prevent pressure and infiltration of groundwater into the test cells. Interior cells are mounted on concrete blocks and leachate drains are attached below the cell bottoms.

The test cells were then readied for waste loading. To minimize the exposure time and more closely simulate actual landfill conditions all test cells were completely loaded and covered within 7 days in each loading period. First, a 15.2 cm thick layer of silica gravel was applied at the bottom of each cell. This serves as a reservoir for leachate and prevents refuse from clogging the drain. Silica gravel was

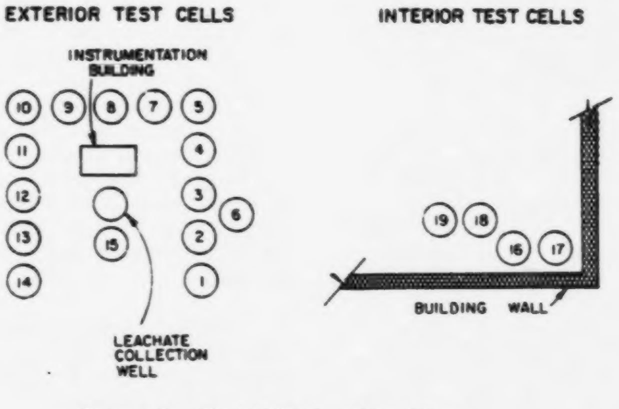

Figure 1. Test Cell Location Plan

selected to prevent any chemical reaction with collected leachate. Refuse was then delivered to the site and added in eight 0.3-m thick increments or lifts. Each lift was compacted with a wrecking ball to a density of approximately 270 kg/m^3. Sludges and other materials added to selected cells were applied to the top of each lift (except the first) in proportionate amounts. No additives were applied to the first lift to avoid any premature leaching of moisture. Temperature probes were installed atop the second, fourth and sixth lifts in each cell. Gas probes were installed atop the second and sixth lifts.

At completion of waste loading a 0.3-m thick layer of silty clay cover soil was applied atop the waste. An additional 0.3-m thick layer of pea gravel was placed atop the cover soil, and a gas probe and water distribution ring installed in the gravel. A settlement indicator was affixed to the top of the gravel and mounted inside a sight glass through the steel lid on each cell. This lid is bolted down to the test cell and caulked to provide an airtight seal. A cross-section of a typical test cell is shown in Figure 2.

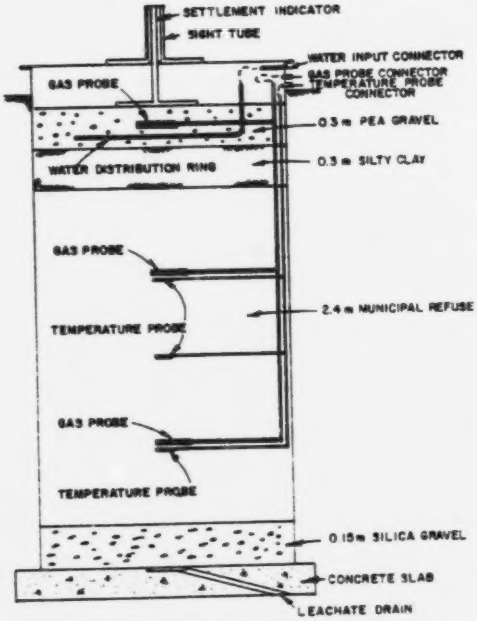

Figure 2. Cross-section of Typical Test Cell

WASTE CHARACTERIZATION

As mentioned previously, sludges and other materials were added to selected cells. These additives are identified in Table 1 along with other pertinent initial loading conditions such as weight and moisture contents. The intent of these additions was to allow an investigation of what effects codisposing these materials with municipal refuse would have on solid waste decomposition. More specifically, this arrangement provided test cells which fulfilled the earlier objectives as follows:

1. Different water infiltration rates: Test Cells 1, 2, 3 and 4.
2. Sewage sludge additions: Test Cells 5, 6 and 7.
3. pH buffer addition: Test Cell 8.
4. Six selected industrial sludge additions: Test Cells 9, 19, 12, 13, 14 and 17.
5. Initial water addition: Test Cell 11.
6. Survivability of poliovirus: Test Cell 15.
7. Different ambient air and soil temperatures: Test Cells 2 and and 16.
8. Duplication of monitoring data: Test Cells 16, 18 and 19.

Before loading, all solid waste for each lift in each cell was weighed and sorted. Eleven sort categories were used and the average composition in each cell was then computed. A summary of the solid waste composition of each cell is shown in Table 2. In addition to categorization, two samples were extracted from each lift. An 11.4 kg sample was used for moisture content determination; these were then averaged over each cell to determine the moisture contents shown in Table 1. An 18.2 kg sample was used for chemical analysis; results were computed for each sort category. A sample composited according to average sort categories in all cells was also chemically analyzed (see Table 3).

OPERATION AND MONITORING

To more closely simulate actual in-field environmental conditions, all test cells are operated in accordance with a strict monthly schedule. First, gas

TABLE 1. TEST CELL LOADING AND OPERATION

Cell Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Refuse																			
wet weight (kg)	3025	2389	3007	3002	3001	2919	2964	2994	3001	2998	2924	3048	3006	3015	1010	2996	2998	3000	3012
moisture content (% of ww)	35	35	35	35	35	35	35	35	32	32	35	35	35	35	32	35	34	32	32
initial moisture (l)	1056	1043	1049	1048	1047	1019	1034	1045	966	965	1020	1064	1049	1052	969	1046	1046	966	970
dry weight (kg)	1969	1946	1958	1954	1955	1900	1930	1949	2035	2033	1094	1984	1957	1963	2041	1950	1972	2034	2042
Additive																			
type	--	--	--	--	sewage sludge	sewage sludge	sewage sludge	$CaCO_3$	petroleum sludge	battery waste	H_2O	electroplating waste	inorganic pigment waste	chlorine prod. brine sludge	polio-virus	--	solvent based paint sludge	--	--
wet weight (kg)	--	--	--	--	68	204	680	90.7	1518	1291	1243.2	1190.4	1420.6	2038.7	--	--	1604.0	--	--
moisture content (% of ww)	--	--	--	--	88	80	98	10	79	89	100	80	51	24	--	--	25	--	--
initial moisture (l)	--	--	--	--	60	179	598	9	1199	1153	1293	946	728	491	--	--	1206	--	--
dry weight (kg)	--	--	--	--	8	25	82	82	319	138	0	244	693	1548	--	--	1206	--	--
Solid Waste Total																			
wet weight (kg)	3025	2989	3007	3002	3069	3123	3644	3084.7	4519	4289	4217.2	4238.4	4426.6	5053.7	3010	2996	4602	3000	3012
moisture content (% of ww)	35	35	35	35	36	38	45	34	48	49	55	47	40	31	32	35	31	32	32
initial moisture (l)	1056	1043	1049	1048	1107	1198	1632	1054	2165	2118	2313	2010	1777	1543	966	1046	1444	966	970
dry weight (kg)	1969	1946	1958	1954	1963	1925	2012	2031	2354	2171	1904	2228	2650	3511	2041	1950	3153	2034	2042
Top Type																			
open									X	X		X	X	X					
open/closed	X	X			X	X	X	X			X				X				
closed			X	X												X	X	X	X
Annual Infiltration																			
mm	203.2	406.4	609.6	812.8	406.4	406.4	406.4	406.4	406.4	406.4	406.4	406.4	406.4	406.4	406.4	406.4	406.4	406.4	406.4
l	533.30	1067.01	1602.95	2135.87	1067.01	1067.01	1067.01	1067.01	1067.01	1067.01	1067.01	1067.01	1067.01	1067.01	1067.01	1067.01	1067.01	1067.01	1067.01

TABLE 2. REFUSE COMPOSITION IN TEST CELLS (2)

Test cell	Food waste	Garden waste	Paper	Plastic, rubber leather	Textiles	Wood	Metal	Glass	Ash, rock and dirt	Diapers	Fines
1	9.5	13.8	37.1	6.2	5.0	1.4	12.2	9.3	3.3	2.5	4.0
2	6.3	21.5	41.5	5.4	4.5	2.2	8.5	9.9	3.3	1.2	3.5
3	11.0	30.2	34.9	8.3	3.3	.3	8.6	5.9	3.4	2.3	2.4
4	5.9	22.6	37.8	6.4	4.1	2.0	5.9	8.8	1.4	3.2	3.5
5	11.3	16.6	41.2	6.9	8.0	1.1	8.0	7.0	1.6	1.8	2.9
6	6.1	25.9	36.5	5.4	1.3	1.6	8.1	9.4	3.5	1.5	3.0
7	5.3	20.3	43.6	6.4	3.4	1.7	9.0	6.4	2.9	2.4	2.8
8	6.6	11.1	53.1	8.3	3.9	1.1	5.8	6.4	1.6	1.6	1.7
9	7.6	17.0	41.3	11.9	2.1	1.9	8.9	5.3	2.8	.9	2.1
10	12.2	8.2	44.0	6.1	4.0	4.4	8.8	7.2	4.7	2.9	3.3
11	8.7	16.2	39.8	5.5	5.6	2.6	8.4	9.0	2.0	2.4	3.4
12	8.2	9.5	46.5	5.3	2.7	1.2	7.7	8.8	6.1	1.5	4.2
13	6.3	20.7	39.1	5.7	4.4	1.4	8.3	7.8	1.8	3.7	2.9
14	9.0	11.1	37.1	6.8	5.6	1.5	9.9	8.2	4.1	4.8	4.1
15	12.7	8.4	42.4	7.3	3.5	2.9	7.1	7.9	4.3	2.8	3.6
16	7.3	16.3	41.8	10.1	3.8	.8	8.9	6.0	1.3	2.7	2.8
17	6.0	15.6	45.7	5.3	6.0	1.4	7.7	6.6	2.7	1.6	2.8
18	6.2	9.8	48.3	6.1	3.3	3.9	9.3	8.4	3.0	2.9	3.4
19	8.5	11.9	43.2	7.5	2.7	1.9	7.4	10.0	1.9	3.0	3.6
Avg.	8.1	15.7	41.8	6.9	4.1	1.8	8.3	7.8	2.9	2.4	3.2
Std. dev.	2.2	5.3	4.5	1.8	1.5	1.0	1.4	1.4	1.3	1.0	.66

* Percent by wet weight

TABLE 3. REFUSE CHEMICAL ANALYSIS (3)

Component	Paper	Garden	Metal	Glass	Food	Plastics, rubber, leather	Fines†	Ash, rocks, dirt	Diapers	Wood	Composite
COD§	0.804	0.815	0.492	0.011	0.754	2.14	0.935	0.040	0.720	0.503	0.520
TKN	0.028	0.171	0.022	0.140	3.09	1.25	0.131	0.119	0.138	0.228	0.247
Total Phosphate	0.048	3.14	2.79	0.049	10.4	1.40	1.97	4.48	2.65	0.103	2.32
Lipids	2.47	3.04	0.420	1.54	13.8	5.02	4.85	1.52	2.26	1.00	2.84
Ash	92.0	36.5	4.85	2.25	41.6	182	49.5	19.6	96.0	77.9	25.8
Crude fiber	21.7	16.6	0.235	0.040	10.5	21.5	6.39	5.85	13.7	20.8	11.3
Total carbon	58.0	14.4	4.80	0.750	19.5	15.8	16.4	13.4	44.5	51.0	24.8
Inorganic carbon	4.30	4.66	3.40	0.220	2.58	5.75	4.30	7.80	0.740	0.380	3.08
Organic carbon	53.7	9.74	1.40	0.530	17.0	10.1	12.1	5.60	43.8	50.7	21.8
Sugar as Sucrose	<0.1	1.71	<0.1	<0.1	6.08	<0.1	1.18	<0.1	<0.1	<0.1	3.50
Starch	3.40	7.42	<0.1	<0.1	8.57	3.42	7.20	6.40	<0.1	0.78	16.2
Asbestos	NA¶	NA	NA	NA	NA	NA	NA	NA	NA	NA	<1**
Arsenic††	<0.1	NA	<0.1	10.2	NA	NA	1.2	3.6	<0.1	<0.1	80
Selenium††	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	<0.1
Mercury††	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	5.0
Lead††	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	15.0
Beryllium††	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	<0.1
Cadmium††	0.36	NA	20.9	2.7	NA	1.855	4.2	4.5	0.25	1.6	2.4
Iron††	375	330	625*	3220	305	444	0.392*	0.340	99.0	0.378	0.782*
Zinc††	50.0	106	175	9.75	59.0	118	322	181	343	59.4	127
Chromium††	8.2	1.1	15.3	1.1	1.3	2.0	13.1	10.1	0.5	1.1	10.7
Manganese††	13.1	194	870	15.7	12.2	12.1	115	177	5.90	50.0	90.5
Potassium††	11.2	0.135*	1.00	2.70	0.162*	98.7	135	555	750	90.0	475
Magnesium††	160	4175	80.5	472	377	289	1.02*	2.63*	279	253	0.225*
Calcium††	77.5	0.830*	<0.25	16.2	0.465*	912	2.11*	4.08*	360	590	0.437*
Sodium††	9.70	185	37.0	60.0	804	143	400	0.209*	0.110*	572	950
Copper††	4.5	9.34	0.221*	2.34	8.58	12.4	35.8	32.6	4.14	38.2	31.6
Nickel††	15.7	15.7	115	19.0	12.5	32.0	33.2	10.1	3.36	27.0	10.1
Moisture	56.7	156.4	8.80	2.00	216.5	57.06	123	30.79	133	21.43	
Moisture¶¶	35.20	56.91	6.18	1.65	70.07	49.27	49.36	18.52	66.28	17.10	
Composition	42.6	10.7	12.2	12.2	3.6	8.7	2.9	3.2	1.3	2.6	
Composition¶¶	41.62	15.77	8.21	7.83	7.56	10.91	3.58	3.36	2.47	1.99	

* Percent by dry weight unless otherwise specified.

† <25.4 mm (1.0 inch).

§ g COD/g sample.

¶ Not analyzed.

** Fibers per gram.

†† Parts per million by weight.

§§ Plastics, rubber, and leather not analyzed.

¶¶ Percent wet weight.

systems on each cell are controlled by top positions. As shown in Table 1, tops may be (1) permanently open as for Test Cells 9, 10, 12, 13 and 14; (2) permanently sealed closed as for Test Cells 3, 4, 16, 17, 18 and 19; or (3) opened and closed in accordance with a monthly schedule as for Test Cells 1, 2, 5, 6, 7, 8, 11 and 15. The schedule of open/closed gas systems is shown in Table 4. These gas systems are closed only during selected months to simulate temporary infield conditions of frozen or saturated ground cover.

TABLE 4. MONTHLY CELL OPERATION SCHEDULE

	Gas System Schedule	Infiltration Schedule				
			Amount per month (liters)			
Month	Position on Open/ Closed Cell Tops	Type per Month	203.2 mm Annual Rate	406.4 Annual Rate	609.6 Annual Rate	812.8 Annual Rate
January	Open	None	0	0	0	0
February	Open	Low	48.52	96.90	145.72	194.17
March	Closed	High	96.90	194.17	291.45	388.34
April	Closed	High	96.90	194.17	291.45	388.34
May	Open	High	96.90	194.17	291.45	388.34
June	Closed	Low	48.52	96.90	145.72	194.17
July	Closed	None	0	0	0	0
August	Open	None	0	0	0	0
September	Closed	None	0	0	0	0
October	Open	Low	48.52	96.90	145.72	194.17
November	Closed	Low	48.52	96.90	145.72	194.17
December	Closed	Low	48.52	96.90	145.72	194.17
Total	--	--	533.30	1067.01	1602.95	2135.87

Secondly, water is applied to each test cell in accordance with the annual infiltration rates listed in Table 1. As shown, with the exception of Test Cells 1, 3 and 4, all test cells receive an annual water application of approximately 400 mm. Test Cells 1, 3 and 4 receive annual applications of approximately 200, 600 and 800 mm, respectively. In this way, the goal of varying the moisture regimen is realized in Test Cells 1, 2, 3 and 4 (with 200, 400, 600 and 800 mm of infiltration, respectively). Water is applied in accordance with the schedule shown in Table 4. As shown, an attempt has been made to duplicate infield conditions. Specifically, high applications are made in the normally rainy months of March, April and May. No applications are made in the normally dry months of January, July, August and September. Low applications are made in the remaining months.

Physical data recording, sampling and analysis are performed in accordance with the schedule in Table 5. To summarize this schedule, gas volumes, refuse temperatures and refuse settlements are recorded regularly. Gas samples are collected each month and analyzed via a gas chromatograph for five major constituents. Leachate samples are collected each month, their volumes recorded, and representative samples prepared. Monthly samples are then analyzed for 22 parameters. An additional 12 parameters are determined quarterly and 7 parameters semi-annually. All analyses are performed at the Center Hill Laboratory using facilities and equipment used exclusively for this project. Strict quality assurance program procedures are utilized to ensure the validity of sampling results. Analytical data derived from the project is punched onto computer cards and entered into the memory banks of an EPA in-house computer. This computational facility can then be used for plotting project data as an aid in evaluating results.

MOISTURE BALANCE EVALUATION

A previous paper(4) on this project addressed the moisture balance for these cells. Figure 3 is a plot of the moisture added and moisture leached for Test Cell 2, which is the control cell for the exterior industrial waste loaded cell comparison. All of the cells loaded with industrial

TABLE 5. DATA RECORDING, SAMPLING AND ANALYTICAL SCHEDULE

SAMPLE	ANALYSIS	TEST CELL	FREQUENCY
Gas	CH_4	All	Monthly
	CO_2	All	Monthly
	N_2	All	Monthly
	O_2	All	Monthly
	H_2	All	Monthly
	Volume	16, 17, 18, 19	Daily
Soil/ Refuse	Temperature	1 - 15	Biweekly
	Temperature	16, 17, 18, 19	Daily
	Settlement	All	Monthly
Leachate	TOC	All	Monthly
	COD	All	Monthly
	Total Solids	All	Monthly
	Total Volatile Solids	All	Monthly
	pH	All	Monthly
	ORP	All	Monthly
	Specific Conductance	All	Monthly
	Alkalinity	All	Monthly
	TKN	All	Monthly
	ortho-PO_4	All	Monthly
	Fe	All	Monthly
	Cd	All	Monthly
	S^-	All	Monthly
	Cl	All	Monthly
	Hg	All	Monthly
	V	2, 4, 10, 13	Monthly
	Be	2, 4, 9, 10, 12, 13, 14	Monthly
	Se	2, 4, 9, 12, 13	Monthly
	CN	2, 4, 10, 13	Monthly
	Phenol	2, 4, 5, 6, 7, 9	Monthly
	As	2, 4, 14	Monthly
	Cr^6	2, 4, 9, 13	Monthly
	Cu	All	Quarterly
	Pb	All	Quarterly
	Ni	All	Quarterly
	Zn	All	Quarterly
	Asbestos	2, 4, 5, 6, 7, 13, 14	Quarterly
	Sn	All	Quarterly
	Ti	2, 4, 14	Quarterly
	Total PO_4	All	Quarterly
	Organic Acids C_2 to C_6	All	Quarterly
	Fecal Coliform	All	Quarterly
	Fecal Streptococci	All	Quarterly
	Cr total	All	Quarterly
	As	All	Semi-annually
	Phenol	All	Semi-annually
	Be	All	Semi-annually
	Tl	All	Semi-annually
	B	All	Semi-annually
	V	All	Semi-annually
	Sb	All	Semi-annually

wastes received the same moisture applications as Test Cell 2. Test Cell 16 was the control for Test Cell 17 comparison.

LEACHATE QUALITY EVALUATION

A total of 41 parameters were measured on leachate samples collected for this project. Thirteen of these were selected for discussion here. It is useful to remember that plots shown depict mass leached (cumulative Kg contaminant/Kg of dry solid waste) as a function of leachate volume (cumulative l of leachate/Kg of dry solid waste).

pH

Figures 4 and 5 are plots of pH as a function of cumulative leachate volume for the control Test Cell 2 and Test Cell 12 which received plating wastes. This is an example of a waste which influenced the pH of the leachate to be generally higher than the control. Usually approximately 0.7 units higher than the pH of the control. Sewage sludge addition did not appear to cause any appreciable change in pH of the leachate. Other industrial wastes which did not appreciably change leachate pH were the chlorine production sludge, paint sludge and water softening sludge. Petrochemical wastes, battery wastes, and inorganic pigment wastes resulted in noticeable higher pH values similar to the plating wastes. So Test Cells 9, 10, 12, and 13 all exhibited leachate pH values that were noticeably higher than the control. This would appear to reflect some toxic effect on the organisms producing acids in the cells, which resulted in less acid production and higher pH values.

Alkalinity

Figures 6 and 7 are alkalinity plots for the control Test Cell 2 and the Battery Production Waste Test Cell 10. These plots illustrate the reduction effects on alkalinity caused by this industrial waste. Note that the control plot is a curve which

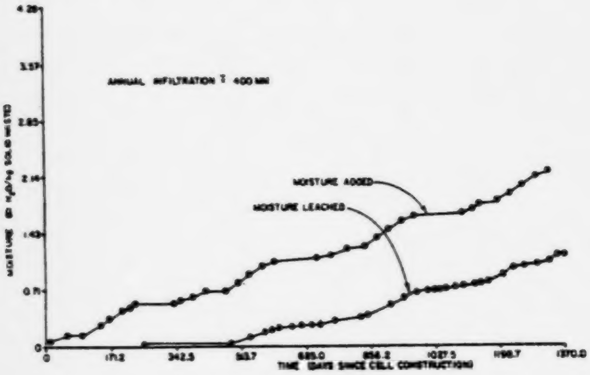

Figure 3. Moisture At Test Cell 2

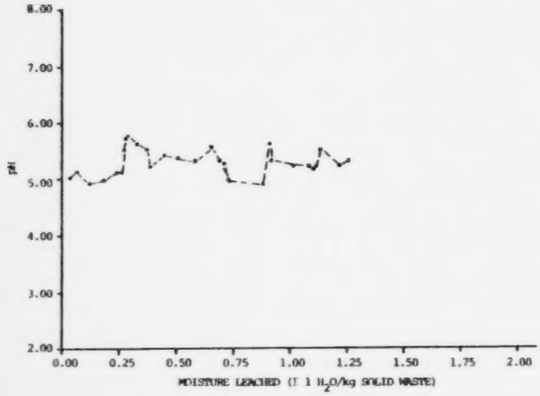

Figure 4. Moisture Leached: pH At Test Cell 2

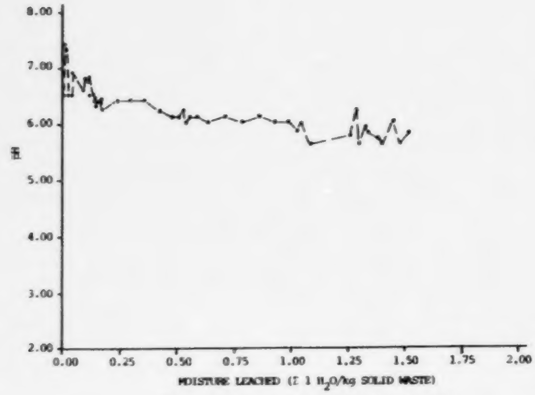

Figure 5. Moisture Leached: pH At Test Cell 12

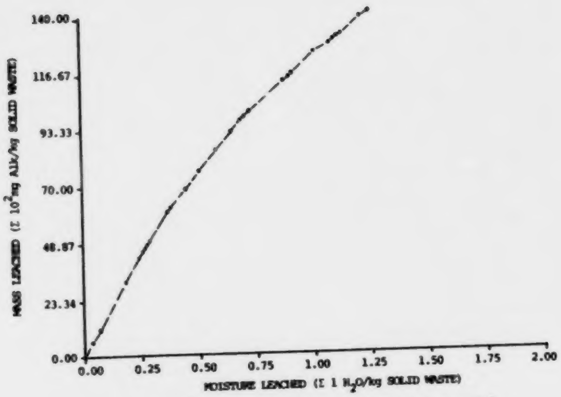

Figure 6. Mass Leached: Alkalinity At Test Cell 2

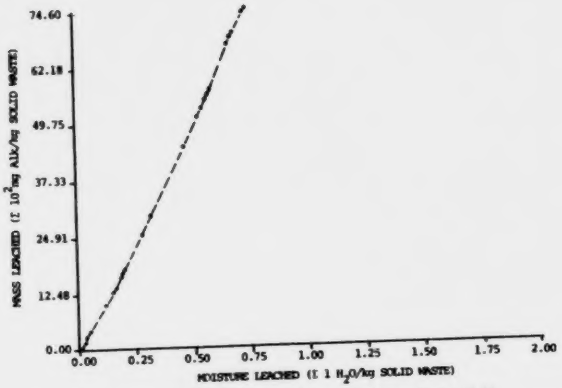

Figure 7. Mass Leached: Alkalinity At Test Cell 10

appears to be approaching an asymptote, but the Test Cell 10 plot has a straight line configuration and the values for alkalinity are considerably lower than the control. This could mean that the industrial waste was retarding decomposition and hence the production of alkalinity in the period presented. Test Cells 8, 9, 13 and 17 exhibited this kind of effect. Sewage sludge in Test Cells 5, 6, and 7 had an opposite effect. An increase in alkalinity was noted in this case. Test Cells containing plating wastes and chlorine brine production waste also exhibited this effect of an increase in alkalinity. Alkalinity is important in methane production and study of the plots reveals that there is considerable alkalinity available to withstand momentary increases in acids without drastic changes in pH.

Total Solids

Total solids release followed the asymptotic configuration in every case. Figures 8 and 9 are plots for Test Cells 2 and 14 respectively. Test Cell 14 had a much higher release of solids than did Test Cell 2. Test Cell 12 also had a greater release of solids than the control. All of the other cells loaded with sewage and various industrial waste had a lower release of solids than the control. Only the plating wastes cell and the chlorine production brine waste cell had a release of solids higher than the control.

Total solids contain both an organic fraction and an inorganic fraction, both of which vary with time from initial placement of the refuse. This makes

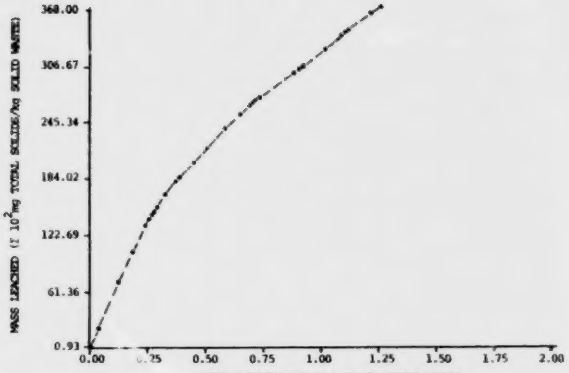

Figure 8. Mass Leached: Total Solids At Test Cell 2

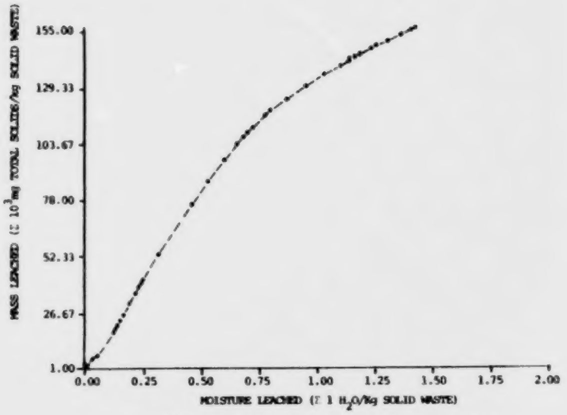

Figure 9. Mass Leached: Total Solids at Test Cell 14

interpretation of why the solids release from one cell is greater than the solids release from another cell difficult, but it appears that in the two cases where the solids levels were greater than the control the greater release resulted from a high contribution of inorganic materials that were amenable to leaching. In all of the other cells where total solids release was less than the control, there appeared to be a slowdown in the rate of solubilization, probably caused by decreased biological activity in the cells and decreased levels of inorganics readily soluble in water. This suggested that the wastes were exerting an effect on biological activity and solids release.

TOC

Total Organic Carbon values were plotted in Figures 10 and 11 for Test Cell 2 and Test Cell 10 respectively. Test Cells 8, 9, and 10 released TOC at a reduced rate when compared with the control. Also the release follows a different pattern as evidenced by the straight line plot in Figure 12 for Test Cell 10 containing battery wastes. The control, Test Cell 2, followed an asymptotic release. Test Cells 12, 13, 14, 17 and the sewage sludge cells followed a release pattern similar to the control. Both major mechanisms of TOC release in the leachate (chemical and biological) were probably affected by the wastes which lowered the release.

COD

Chemical Oxygen Demand values were plotted in Figures 12 and 13 for Test Cell 2 and Test Cell 10 respectively. COD was released at a reduced rate by Test Cells 8, 9, 10 and 13. Release followed a similar asymptotic configuration as the

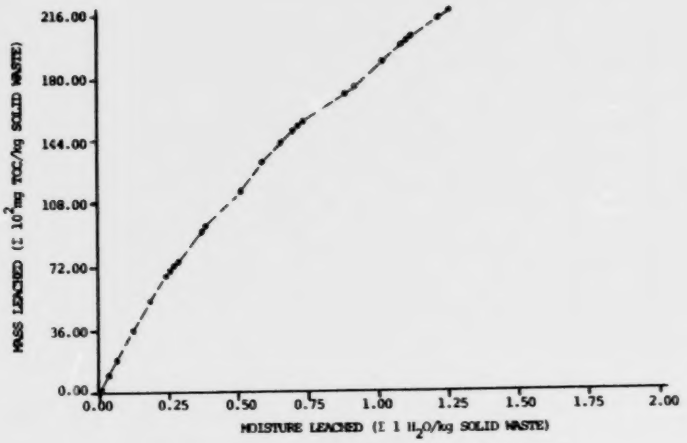

Figure 10. Mass Leached: TOC At Test Cell 2

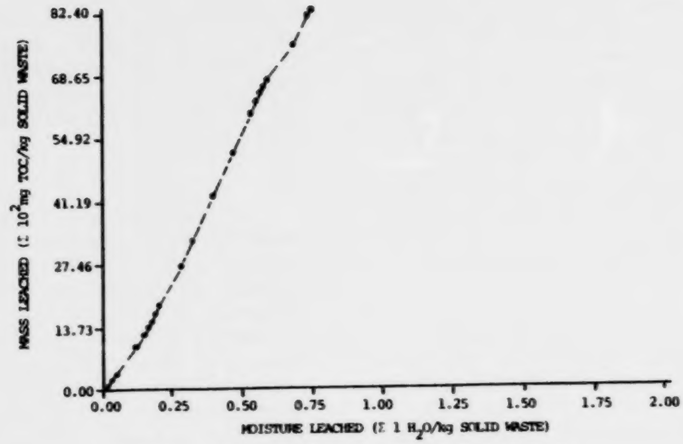

Figure 11. Mass Leached: TOC At Test Cell 10

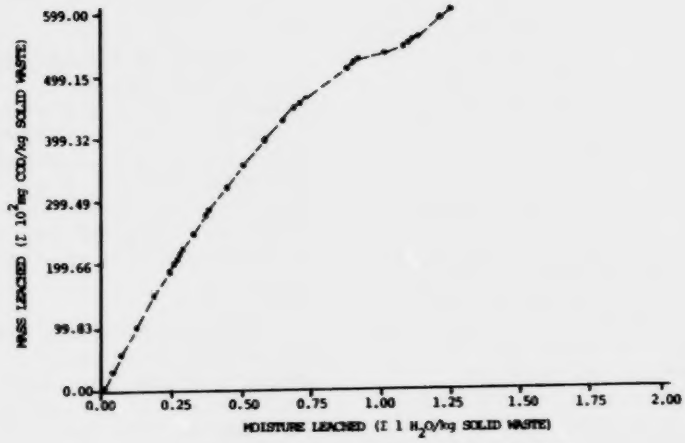

Figure 12. Mass Leached: COD At Test Cell 2

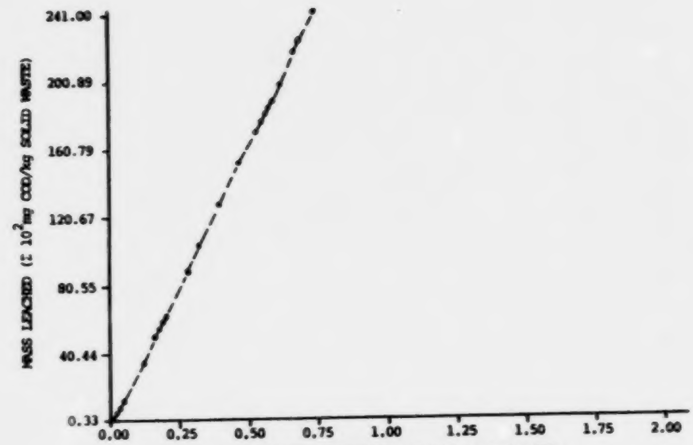

Figure 13. Mass Leached: COD At Test Cell 10

control with the exception of Test Cell 10, which followed a straight line release at a much lower rate. COD values that are higher than most parameters on a mg/l basis result from the many organic and inorganic substances in the refuse leachate amenable to chemical oxidation in this test. Test Cells 8 and 10 ($CaCO_3$ and battery wastes respectively) showed less TOC release and COD release than the controls. Test Cells 5, 6, 7, 12, 14 and 17 had COD release similar to the control.

TKN

Total Kjeldahl nitrogen release followed an asymptotic pattern. Figures 14 and 15 represent the control, Test Cell 2, and Test Cell 8 containing the softening sludge. Note that the release from Test Cell 8 was significantly lower than the control. This was characteristic of Cells 9, 10, 12, and 13. Substances in these cells may have interferred with the biological denitrification reactions. All of the other cells 5, 6, 7, 14, and 17 had approximately the same release of this form of nitrogen. Note that the sewage sludge addition had little effect on this important leachate parameter.

Metals: Fe, Cu, Cr, Pb, Ni, Cd, Zn, Hg

Eight metals were selected for review here. In general the release of metals followed three types of curves or combinations thereof. Either a straight line release or series of straight line releases was a common configuration. Another was the familiar curve approaching an asymptote with a decreasing rate of increase. The third type was a curve with an increasing rate of increase. Many mechanisms work in a landfill to cause the release of specific metals in the leachate. It appears that any metal no matter what its theoretical solubility in water, may be leached from the refuse over a period of time.

Fe

Figures 16 and 17 depict the mass release of iron for Test Cell 2 and Test Cell 14 respectively. The straight line release in Figure 16 is typical for Test Cells 5, 6, 7, 8, 9, 10, 12, 13 and 17. Figure 17 depicts the mass release for Test Cell 14 and has an increasing rate of increase type of release. Release from Test Cells 8, 12, 13, 14 and 17 was less than the control. These wastes appeared to slow down the release of iron. Two of the sewage sludge Cells, 6 and 7, had greater releases of iron.

Cu

Figure 18 depicts the mass release of copper from Test Cell 2. All of the Cells released copper in a similar manner. Cells 9, 12 and 14 released more, while Cells 8, 10, and 13 released less. Sewage sludge in Cells 5, 6 and 7 did not appear to affect any change in release of copper. Copper was released from different locations in the cells at different rates.

Cr

Figure 19 depicts the mass release of chrome from Test Cell 2. All of the Cells released chrome in a similar manner. Each Cell containing industrial waste released less chrome than the control Cell. Chrome was present in the leachate in sub-mg/l

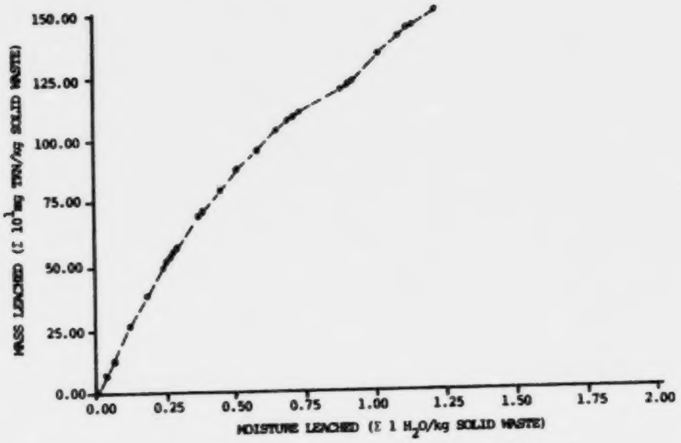

Figure 14. Mass Leached: TKN: At Test Cell 2

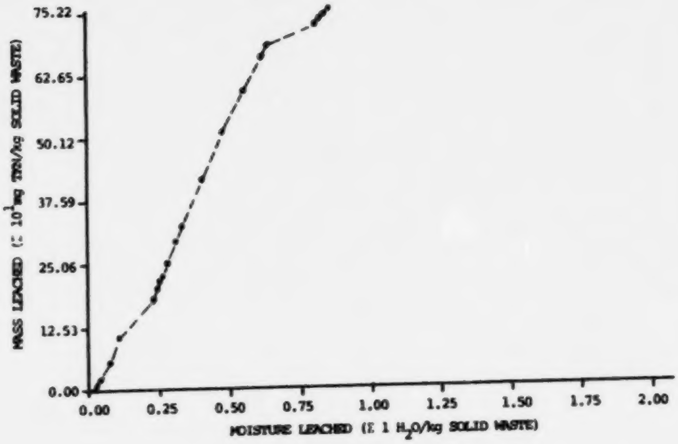

Figure 15. Mass Leached: TKN At Test Cell 8

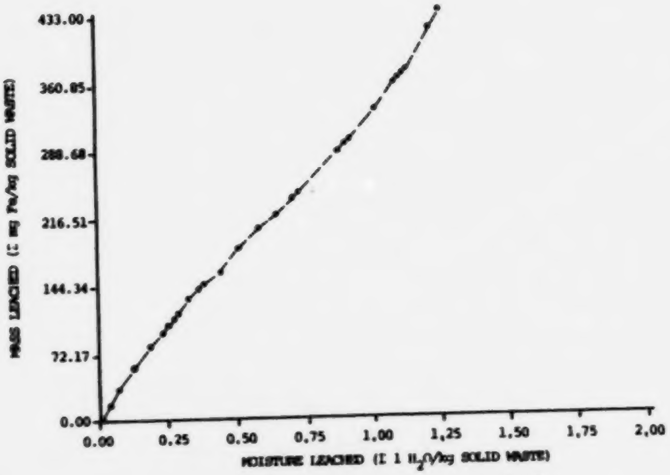

Figure 16. Mass Leached: Fe At Test Cell 2

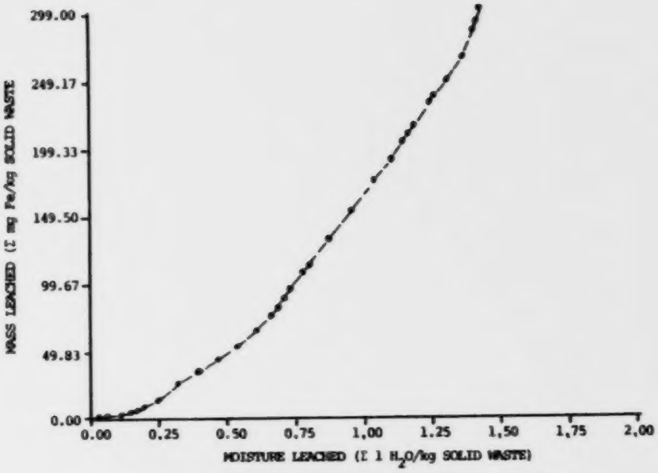

Figure 17. Mass Leached: Fe At Test Cell 14

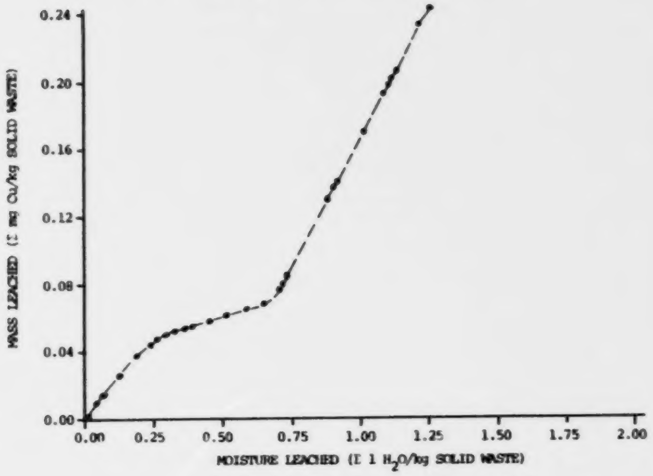

Figure 18. Mass Leached: Cu At Test Cell 2

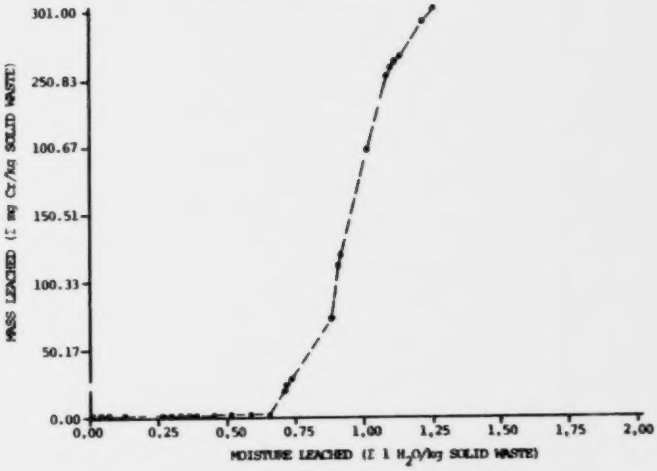

Figure 19. Mass Leached: Cr At Test Cell 2

concentrations only. Chrome release from landfill refuse appeared to be a slow process.

Pb

Figures 20 and 21 depict the mass release of lead from Test Cells 2 and 12 respectively. Test Cells 8, 9, 10, 13 and 17 had higher releases of lead than the control. Note in Figure 21 the increasing rate of increase with time for lead release.

Ni

Figures 22 and 23 depict the release of nickel from Test Cells 2 and 12 respectively. Note that the control was asymptotic, while the cell containing the electroplating wastes had different rates of release and a higher total release to date. Only Test Cells 12 and 14 released nickel at higher values than the control. Test Cells 5, 6, 7, 8, 9, 10, 13 and 17 released nickel at either the same or lower values as the control.

Cd

Figures 24 and 25 depict the release of cadmium from Test Cells 2 and 10 respectively. Note the straight line release pattern and the different rates of release. Only the battery wastes in Test Cell 10 showed a higher release of cadmium than the control. Test Cells 5, 6, 7, 8, 9, 12, 13, 14 and 17 released cadmium at either the same or slightly lower values as the control.

Zn

Figures 26 and 27 depict the release of zinc from Test Cells 2 and 17 respectively. Release followed an approximate asymptotic configuration. All of the Test Cells released zinc at either the same rate or a lower rate than the control to date.

Hg

Figures 28 and 29 depict the release of mercury from Test Cell 2 and 14 respectively. Both curves follow an approximate asymptotic configuration. All of the Test Cells containing industrial wastes released mercury at either the same or a lower rate than the control. Only Test Cell 14 released more mercury than the control. Release from this cell containing the chlorine production brine sludge was over twice as much as from Test Cell 2. This waste would be expected to contain some residual mercury from the mercury cells used in chlorine production. So the release values were not unexpected.

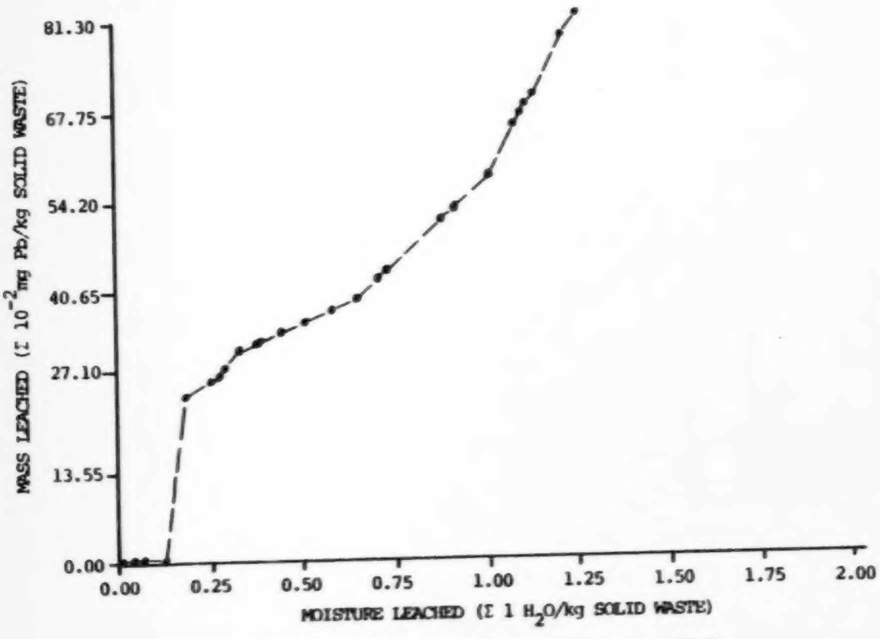

Figure 20. Mass Leached: Pb At Test Cell 2

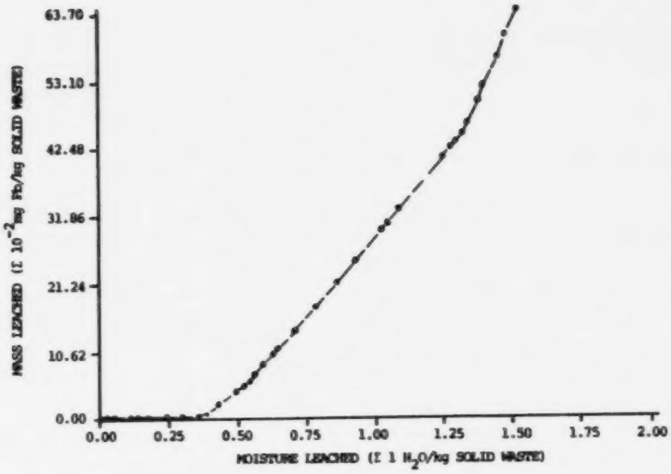

Figure 21. Mass Leached: Pb At Test Cell 12

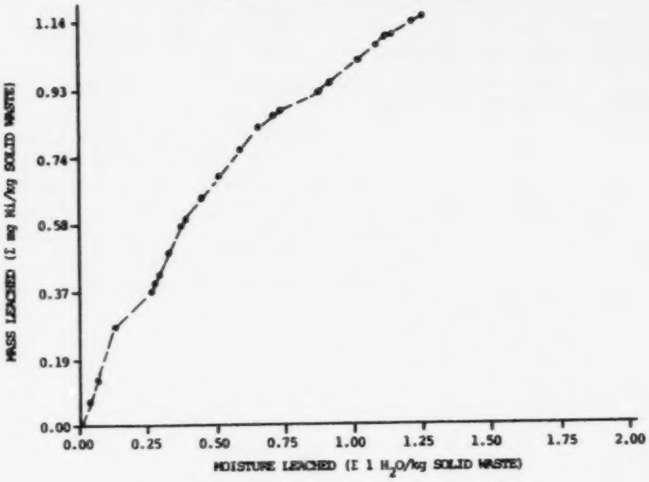

Figure 22. Mass Leached: Ni At Test Cell 2

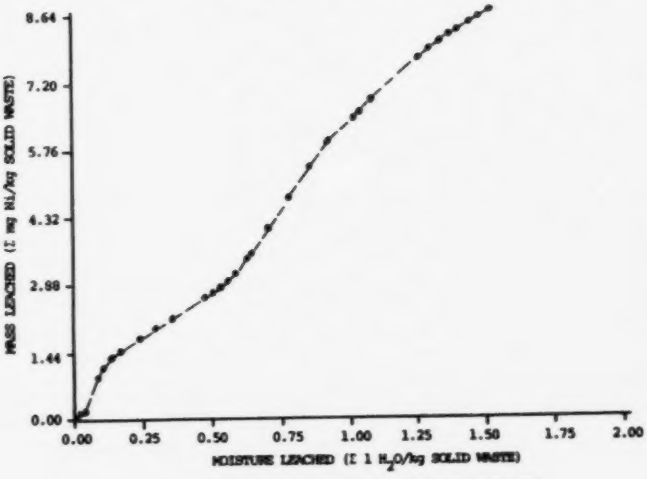

Figure 23. Mass Leached: Ni At Test Cell 12

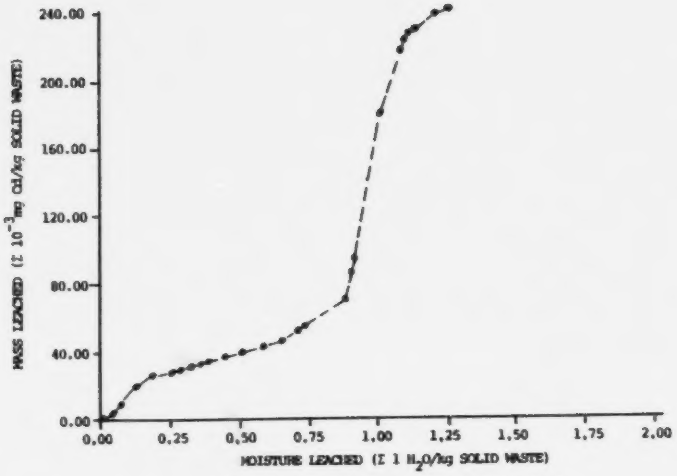

Figure 24. Mass Leached: Cd At Test Cell 2

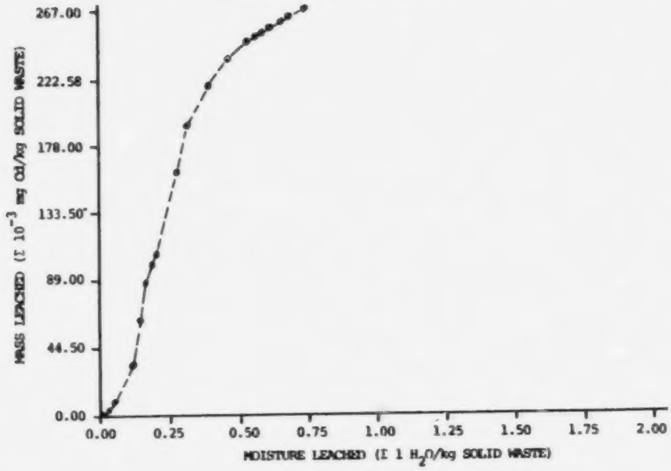

Figure 25. Mass Leached: Cd At Test Cell 10

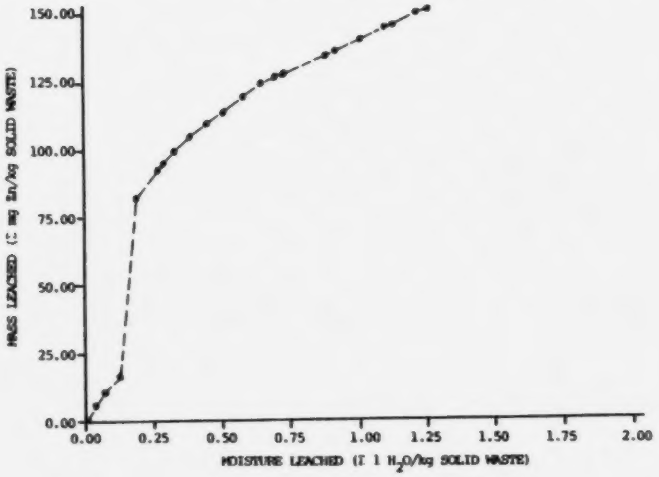

Figure 26. Mass Leached: Zn At Test Cell 2

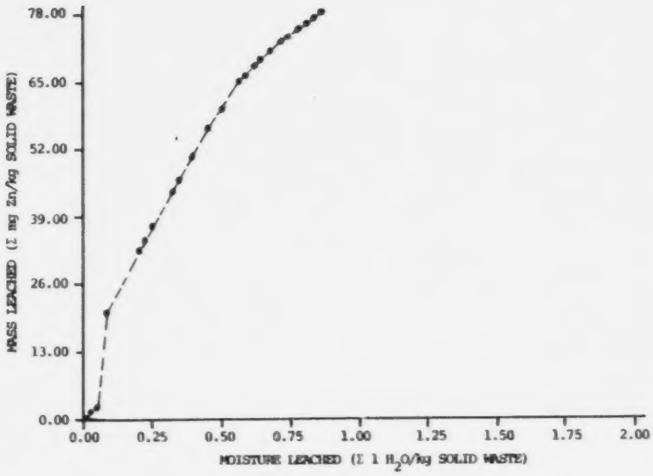

Figure 27. Mass Leached: Zn At Test Cell 17

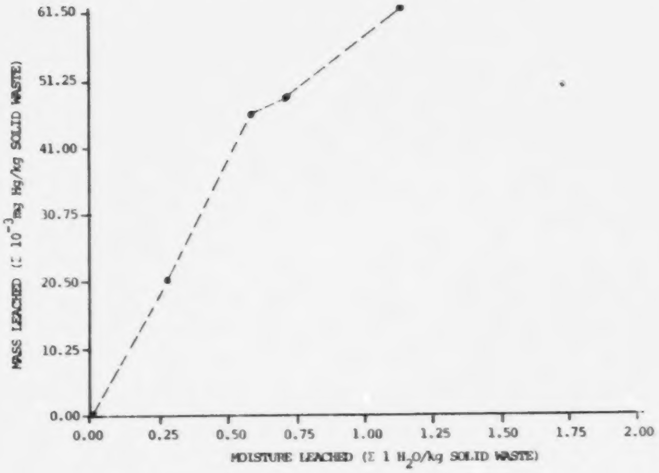

Figure 28. Mass Leached: Hg At Test Cell 2

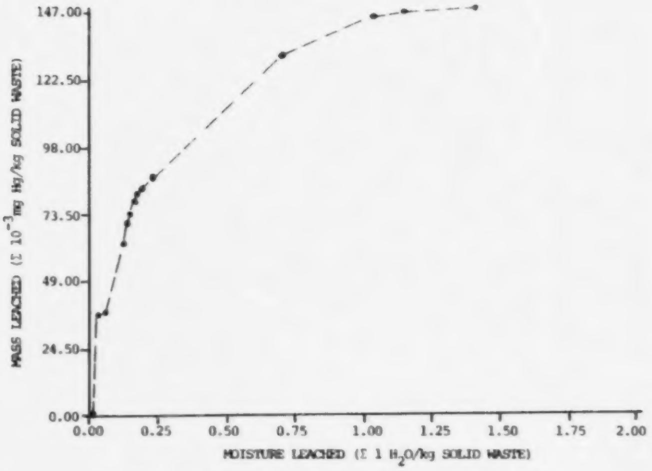

Figure 29. Mass Leached: Hg At Test Cell 14

GAS EVALUATION

Gas samples were extracted from all test cells on a monthly basis for CH_4, O_2, CO_2, and N_2 analyses. Gas quantity data were recorded for the interior cells 16, 17, 18 and 19 on a daily basis. Figures 30 and 31 depict the quantity of gas generated at Test Cells 16 and 17. Gas volumes from Test Cell 17 with the solvent based paint sludge do not appear to be greatly different from the control Test Cell 16.

Figures 32 and 33 depict the methane composition in the gases from these same two cells. Percent methane appeared to be higher in the solvent based paint sludge cell for most of the time period with the exception of the initial days of gas production. It appeared the toluene xylenes etc. were readily amenable to conversion to methane.

ACKNOWLEDGEMENTS

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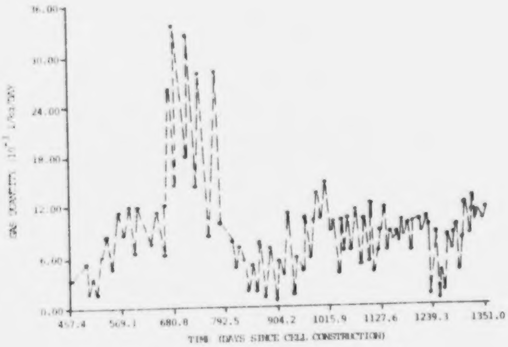

Figure 30. Gas Quantity At Test Cell 16

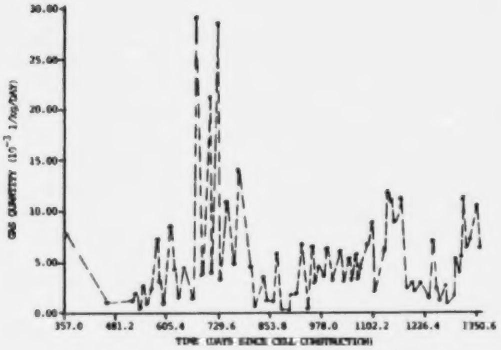

Figure 31. Gas Quantity At Test Cell 17

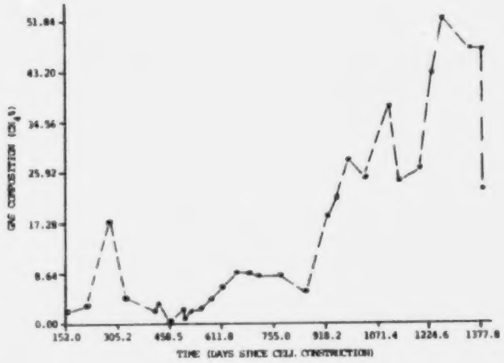

Figure 32. Methane Gas At Test Cell 16

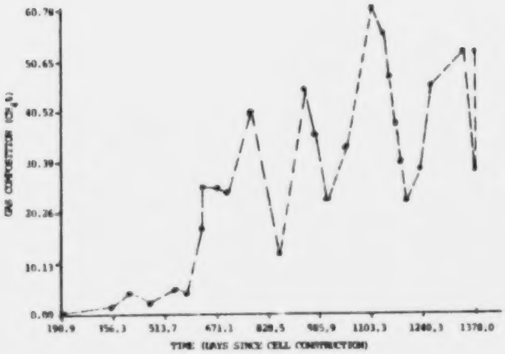

Figure 33. Methane Gas At Test Cell 17

CHEMICALLY STABILIZED INDUSTRIAL WASTES IN A SANITARY LANDFILL ENVIRONMENT

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ABSTRACT

Simulation of the co-disposal of municipal solid waste (MSW) with untreated industrial waste and with chemically stabilized industrial wastes in large-scale test cells was initiated in April 1978. Simulations were conducted in 1.83 x 3.66 m cylindrical test cells designed to simulate sanitary landfill environments. Three industrial wastes were chemically stabilized by two commercially available processes. The three types of industrial wastes were electroplating sludge, chlorine production brine sludge, and calcium fluoride/ sewage sludge. All test cells received deionized water equivalent to an infiltration rate of 66 cm per year. Leachate samples were collected and analyzed for 10 parameters on a monthly basis and extensive chemical characterization of leachates for 17 metals was conducted on a quarterly basis. Results of these analyses for the first 9 months of leachate production are compared to control test cells containing MSW only. Release of toxic metals from untreated chlorine production brine sludge co-disposed with MSW was observed, however, chemical stabilization significantly reduced the leaching of toxic metals from the co-disposed chlorine production brine sludge. The co-disposal of treated or untreated electroplating sludge with MSW did not affect typical leachate quality. The co-disposal of MSW with calcium fluoride/sewage sludge apparently improved leachate quality.

INTRODUCTION

Since passage of the Resource Conservation and Recovery Act of 1976 (RCRA), regulation of the disposal of solid and hazardous waste has become a top priority of the EPA. As increasing amounts of solid and hazardous waste are directed to the land for disposal, concern about the adequacy of protection for the environment and human health has played a major role in establishing regulations and guidelines under RCRA. Reports of improperly disposed chemical waste and leaking landfills have made nationwide news during the past year. As a result, an extensive hunt or survey has been launched by the EPA to identify waste disposal sites for the purpose of assessing the magnitude and severity of problems associated with solid and hazardous waste disposal under RCRA.

Oftentimes sanitary landfills have received industrial wastes at some time during their operation. Inadequate records of landfill operation and the absence of indicators of industrial waste pollution, have lead to the misconception that pollution problems from sanitary landfills are due primarily to contaminants released by the decomposing municipal solid waste (MSW). Thus, information on the transformation and mobility of industrial waste co-disposed with MSW is needed in order to determine whether the quality of leachate from sanitary landfills is effected.

Previous studies reported by Newton,[1] Streng,[2] Swartzbaugh et al.,[3] and Walsh and Kinman,[4] have dealt with the effects of untreated industrial sludges on leachate quality when co-disposed with MSW. Newton concluded that the presence of industrial wastes (an oil/water emulsion, metal hydroxide sludge, and cyanide waste) except in the case of the cyanide waste, did not effect the composition of the MSW leachate. Other researchers[2,3,4] concluded that the addition of industrial wastes evaluated in their studies appeared to have little effect on organic, nutrient and other demand parameters; whereas, metallic ion concentrations within the leachate may be affected depending on the chemical composition of the industrial waste itself.

The purpose of this paper is to present preliminary findings from a large scale simulation of the co-disposal of MSW with untreated industrial sludge and with chemically solidified/stabilized industrial sludge. This paper is the first in a series of reports to be published by the EPA, presenting the results of this study.

MATERIALS AND METHODS

Test Cell Construction

The eleven test cells used for this project are housed in a large-scale testing facility (Figure 1) at the U. S. Army Engineer Waterways Experiment Station in Vicksburg, Mississippi. This facility is temperature regulated to maintain 25 ± 3° C for the duration (4 years) of this project. The test cells are cylindrical, steel (6.35 mm rolled plate) tanks with a coal-tar epoxy coating on all interior surfaces. The acid- and base-resistant, coal tar epoxy protects the cell walls from corrosion and the cell contents from contamination. The nine co-disposal test cells and two control (MSW) test cells used in the study have dimensions of 1.83 m inside diameter and 3.66 m in height. The test cells are equipped for collection of leachate samples and insitu measurements of temperature and redox potential.

Test Cell Profiles

Figure 2 is a schematic diagram of the profile of the co-disposal test cell containing chemically stabilized industrial sludge. This profile, as are all the test cell profiles, is built on a base of polypropylene beads overlain by a 30.5 cm layer of sandy soil. The soil is 80 percent sand, 4 percent silt, and 16 percent kaolinite clay. While still at its natural moisture content of 7 percent, the soil was compacted to a dry density of 1763 kg/m^3. Each layer of chemically fixed industrial sludge is composed of four cylinders or cores of fixed sludge. Figure 3 is a picture of four cores of chemically fixed sludge placed over a lift of the MSW. During the loading operation MSW was packed around the cores to a density of 400 kg/m^3 (wet wt). The profile was completed with a 7.6 cm layer of washed pea gravel. The pea gravel provides a relatively inert cover that reduces evaporation and assists in the distribution of the infiltrate. The test cell lid was tack welded at 15 cm intervals to the flange around

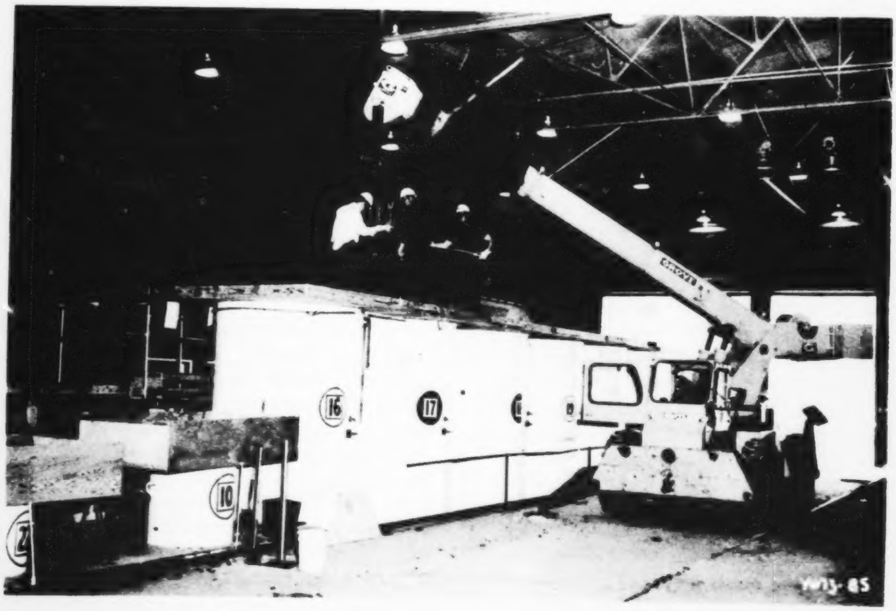
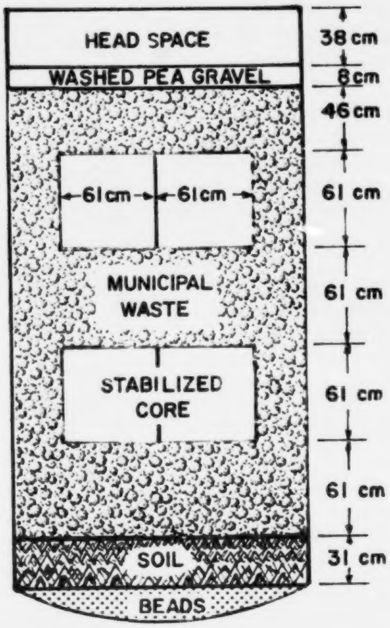


Figure 1. Facility for housing co-disposal test cells.


HEAD SPACE
38 cm
WASHED PEA GRAVEL
8 cm
46 cm
61 cm
61 cm
61 cm
61 cm
61 cm
61 cm
MUNICIPAL WASTE
STABILIZED CORE
61 cm
SOIL
31 cm
BEADS

Total Municipal Waste = 7.64 cu. yd.
Total Stabilized Sludge = 1.86 cu. yd.
Municipal Waste : Stabilized Sludge ≈ 4.1:1 vol/vol

Figure 2. Schematic diagram of typical co-disposal test cell profile.

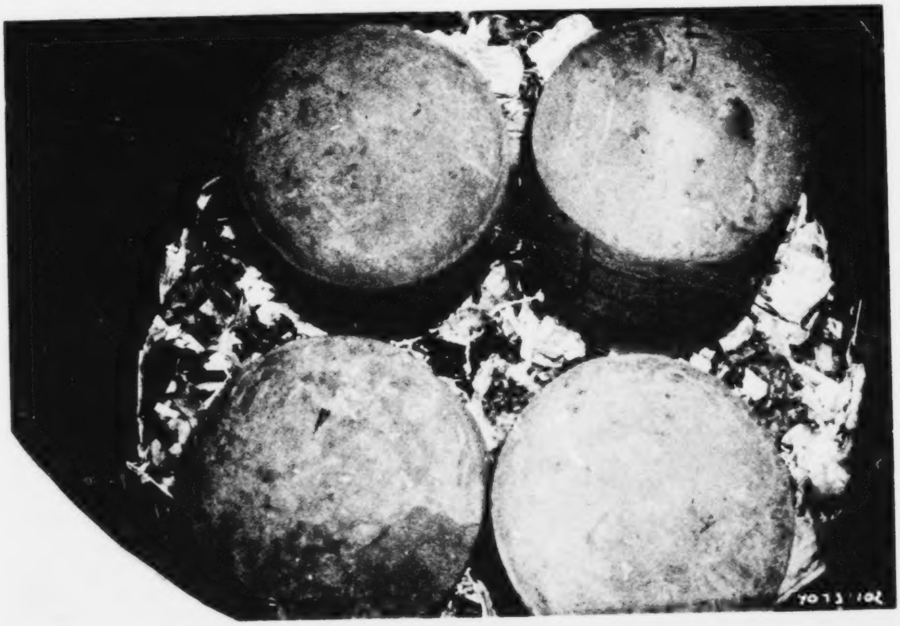


Figure 3. Placement of chemically stabilized cores in test cell.

the top of the test cell and the small cracks (1 mm) that occurred between some welds were filled with metal sealant.

The co-disposal test cell profiles containing the untreated industrial sludges are the same as those containing the stabilized cores except that the cores are replaced with a layer of untreated industrial sludge.

The control (MSW only) test cell profile was constructed to resemble a core of MSW taken from a municipal landfill of medium density in the humid eastern United States.

Test Cell Compositions

Waste Descriptions -

Table 1 shows the weights of co-disposed material and MSW contained in the test cells.

All MSW was obtained from non-commercial collection routes in Warren County, MS, in April 1978. A 500-kg composite sample of MSW was sorted at the time the test cells were filled and the resulting percent composition of the MSW used in the study is given in Table 2. Table 2 also presents composition data from other leaching studies.

Three industrial sludges were selected from the five studied by Mahloch et al[8]. This study used the same sludge sources and sludge numbering system used by Mahloch. Sludge selection was based on availability, potential hazard if co-disposed with MSW, and the potential applicability of chemical stabilization as a disposal pretreatment process.

Sludge 200 is an electroplating waste. The sludge generator discharges separately treated wastes from plating, phosphatizing and metal cleaning operations to a series of lagoons. Solids settle in the first

TABLE 1. TEST CELL CONTENTS

	Test Cell No.	Sludge Type	MSW Kg, Dry Wt	Co-disposed Material Kg, Dry Wt
Untreated	19	200	2035	704
	20	800	2041	1678
	21	900	2039	1303
Process A	14	200	2038	1951
	17	800	2036	2609
	18	900	2045	2026
Process B	11	200	2028	2371
	12	800	2043	2302
	13	900	2031	2282
MSW only	15	--	2038	None
	16	--	2096	None

TABLE 2. PERCENT COMPOSITION OF MUNICIPAL SOLID WASTE USED IN THIS AND OTHER INVESTIGATIONS

Category	This Study	Jackson & Streng (5)	Chian and others(6)	Eifert & Swartzbaugh (7)
Paper	44.79*	40.53	36.5	49.6
Metal	10.82	8.29	14.7	9.5
Plastics rubber, leather	9.03	6.52	2.8	6.0
Glass	7.61	7.42	6.8	12.0
Textiles	3.08	4.19	0.7	3.2
Disposable diapers	2.68	1.78	--	1.4
Food waste	0.94	7.53	14.4	7.3
Wood	0.49	0.86	--	--
Garden waste	0.41	15.32	3.1	4.6
Ash, rock, dirt, fines	20.15	5.48	14.9	5.4

* All percentages are on a dry wt. basis.

lagoon which is allowed to evaporate every summer so that dried sludge can be removed to a confined disposal area. Chromium and copper are the primary contaminants in this bright green, clay-like material.

Sludge 800 is chlorine production brine waste. The sludge generator manufactures chlorine gas and caustic soda in a mercury cell process. Sludge from clarifiers in the chlorine and alkali operations is removed to a confined disposal area. The primary contaminants in the tan, granular material are mercury and various alkali salts.

Sludge 900 is clacium fluoride/sewage sludge generated by an electronic manufacturer. An acidic fluoride waste stream and the generator's sewer separately enter the company's wastewater treatment plant and there undergo separate treatment. The sludges that result from physical-chemical treatment of the fluoride waste stream and biological treatment of the sewage are combined in a confined disposal area. The primary contaminants in this light brown material are calcium fluoride and domestic sewage sludge.

Bartos and Palermo[9] have reported on the physical and engineering properties of these sludges and chemical characterization of the sludges is presented elsewhere (Myers et al[10]).

Chemical Solidification/Stabilization Processes -

Separate cement-based (Process A) and pozzolan (Process B) processes were used to treat the industrial sludges selected for this study (Table 3).

Process A, a patented technology, uses two additives to produce a hard, concrete-like material. The additives and waste are dispersed with water in a slurry prior to casting and solidification.

Raw sludge was slurried with a specified amount of water in a rotary pan turbine

TABLE 3. FORMULATIONS FOR SLUDGE SOLIDIFICATION/STABILIZATION

Process	Sludge	Additive/Sludge*	Added Water† percent
A	200	1.630	52.5
	800	0.64	13.9
	900	0.90	15.8
B	200	3.26	0.1
	800	2.14	6.9
	900	5.44	18.5

* Dry weight basis.

† As percentage of total dry weight.

mixer in 0.38 m^3 batches. After the processor was satisfied that all the lumps of sludge had been dispersed and the suspension was homogeneous, the first ingredient was added to the batch one scoop at a time. A second ingredient was added in 40 kg bag increments. After the additives were mixed (usually 3-8 min), the discharge gate on the bottom of the mixer was opened and the treated sludge dumped into a 0.61 x 0.61 m cylindrical cardboard (paraffin impregnated) mold. The molds were mounted on wooden pallets to facilitate removal by a fork lift to a storage area for a curing time of 28 days. The molds were labeled and covered with plastic after being placed in the storage area. Additive to sludge ratios and percentages of water used in the stabilization of each sludge by Process A are listed in Table 3.

Process B uses flyash and other additives to produce a pozzolan type product.

Raw sludge was loaded into the mixer in the same manner as described for Process A. After a predetermined weight of sludge was in the mixer, required amounts of water were added. While the mixer was running, 32 kg bags of the first additive were dumped into the mixer, one bag at a time. Then if additional water was needed to maintain a slurry, more was added. Other Process B additives were then added one scoop at a time. After mixing for approximately 5 min the discharge gate on the bottom of the mixer was opened and treated sludge fell into a pallet-mounted mold. Treated sludge was compacted in the mold in four layers using a hand tamp. The surface of each preceeding layer was scarified before the next layer was packed. The top layer was molded to effect a dome shape for the top of the core. After compaction was finished a plastic cover was taped over each mold and the molds were set in the storage area to cure for 28 days. Two molds were filled per batch. Sludge weights, additive quantities, and amounts of water used in the stabilization of each sludge by Process B are listed in Table 3.

After the specified 28-day curing time eight molds of each sludge type for each process were selected from the available cores. For selected cores the molds and bottom pallets were removed. During the operation the cores were examined for soft spots, fissures, scars, and other obvious signs of poor stabilization or damage. None were found. For loading into the test cells the cores were rigged with nylon nets fastened to iron lifting rings.

Leachate Collection and Analysis

After loading was completed on April 16, 1978, the test cells were sealed and leaching began. Infiltration in each test cell is simulated by applying 66 cm of deionized water per year (at a rate of 1.27 cm per week). The details of the loading operation, provisions for leaching and sample collection, and measurement of cell temperature and redox potential are described in a construction report.[10]

Separate leachate samples from ports above and below the soil layer were collected. Samples collected on a monthly basis were analyzed for 10, select parameters and samples collected on a quarterly basis were analyzed for the entire list of 29 parameters shown in Table 4.

Monthly samples were pumped from the above soil leachate port with a peristaltic pump and were prepared for analysis as given in Table 4. Quarterly samples were collected in a similar manner except that they were prepared in a glove box under an inert atmosphere without oxygen reaching the leachate. This procedure was found necessary in order to avoid sample deterioration between the time of sample collection, subsample preparation, and chemical analysis.

TABLE 4. SAMPLE WORKUP

Subsample	Type	Preparation*
Alkalinity, pH, conductivity	Monthly and quarterly	No preparation; analyze immediately
Chloride	Monthly and quarterly	Store at 4°C, analyze within 48 hr
Mercury	Monthly and quarterly	No preparation; initiate analysis with 4 hr by sealing sample in digestion vessel
Total organic carbon	Monthly and quarterly	No preparation; initiate analysis with 4 hr by sealing sample in digestion ampule.
Cd, Cr, Fe, and Zn	Monthly and quarterly	Dilute 100 ml to 250 ml and preserve with 2.5 ml of Ultrex HNO_3; analyze within 30 days.
Biochemical oxygen demand (5 day)	Quarterly only	Dilute 1 ml to 500 using distilled water.**
Chemical oxygen demand	Quarterly only	Dilute 0.5 ml to 50 ml using distilled water.**
Total volatile acids	Quarterly only	To pH 21.0 using H_2SO_4 and Thymol blue indicator; store at 4°C. analyze within 48 hr.
Fluoride	Quarterly only	No preparation; analyze within 8 hr.
TKN, TP	Quarterly only	Dilute 10 ml to 100 ml; preserve with 1 ml of H_2SO_4. Analyze within 48 hr.**
Al, As, B, Be, Ca, Cu, Pb, Mg, Mn, Ni, K, Se, Na	Quarterly only	Included in Cd, Cr, Fe, and Zn subsample; analyze within 90 days.**

* All quarterly subsamples are collected under a He atmosphere.

** Performed under He atmosphere.

Alkalinity, pH, conductivity, BOD, and COD were run immediately after sample collection. Total volatile acid (TVA) and chloride samples were analyzed within 48 hours of sample collection. Mercury, fluoride and total organic carbon (TOC) analyses were performed within 4 hrs of sample collection. Metals were preserved by adding Ultrex nitric acid to 1 percent acid by volume and analyzed within 60 days. The total Kjeldahl nitrogen and total phosphorous subsamples were preserved with sulfuric acid and analyzed within 48 hrs. The methods used in analyzing the prepared leachates are summarized in Table 5.

To obtain assurance within the analytical program a quality control program including replicate determinations, spiked samples, and referee samples was implemented. Internal control consists of replicate determinations and spiked addi-

TABLE 5. METHODS OF ANALYSIS

Parameter	Procedures and/or instrumentation*	Lowest reporting concentration (ppm)
Specific Conductance	YSI model 31 conductivity bridge	0.5 μmhos
ALK	Standard acid titration†	25
Cl	Destruction of organics using H_2SO_4 and H_2O_2; filter; potentiometric titration with $AgNO_3$, Cl^- electrode, and Metrohm model F536 recording titrator‡	10
TKN	Technicon II Auto Analyzer, Industrial Method 376-75W/B and 32974W/B#	0.01
TP	Same as above	0.01
TOC	Determined with Oceanography International Corp. Model No. 0524B TOC Analyzer	1
Ca	Determined with a Spectrametrics Argon Plasma Emission Spectrophotometer Modell II	0.03
Fe	Same as above	0.003
K	Same as above	0.05
Mg	Same as above	0.03
Mn	Same as above	0.001
Na	Same as above	0.03
Al	Same as above	0.01
As	Determined with a Perkin-Elmer Heated Graphite Atomizer Atomic Absorption Unit	0.001
B	Determined with a Spectrametrics Argon Plasma Emission Spectrophotometer Model II	0.02

(Continued)

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* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

† Standard Methods for the Examination of Water and Wastewater, American Public Health Association, New York, 14th Edition, 1975.

‡ Compilation of methodology for measuring pollution parameters of landfill Leachate. E.S.K. Chain and F. B. Dewalle. EPA-600/3-75-011 October 1975.

# Technicon Industrial Systems, Tarrytown, New York.

TABLE 5. (Concluded)

Parameter	Procedures and/or instrumentation	Lowest reporting concentration (ppm)
Be	Same as above	0.0005
Cd	Determined with a Perkin-Elmer Heated Graphite Atomizer Atomic Absorption Unit	0.0003
Cr	Same as above	0.003
Cu	Same as above	0.003
Hg	Determined by standard cold vapor technique†	0.0002
Ni	Determined with a Perkin-Elmer Heated Graphite Atomizer Atomic Absorption Unit	0.005
Pb	Same as above	0.002
Se	Same as above	.005
Zn	Determined with a Spectrametrics Argon Plasma Emission Spectrophotometer Model II	0.014
BOD_5	Standard 5-day Biochemical Oxygen Demand, unseeded†	2.0
COD	Standard dichromate/H_2SO_4 reflux†	50.0
TVA	Standard column partition chromatographic method†	30.0
pH	Electrometric	--
F	Techicon II Auto Analyzer, Industrial Method 129-71-W	0.04

† Standard Methods for the Examination of Water and Wastewater, American Public Health Association, New York, 14th Edition, 1975.

tions to representative samples. Analysis by standard addition using three separate levels of addition, each addition level run in triplicate, was used to assure quality results from the heated graphite atomizer atomic absorption unit. The interlaboratory control program consists of analysis of performance evaluation samples submitted by the Environmental Monitoring and Support Laboratory, U.S.E.P. A. Cincinnati, OH.

RESULTS AND DISCUSSION

The results from the simulation of the co-disposal of MSW with untreated industrial waste and with chemically stabilized industrial waste represent a 9 month leaching period. The data for the quarterly sample analyses represent 3 sampling periods. Leaching data for the monthly parameters analyzed represent 9 sampling periods. The rationale for selecting the parameters for monthly analysis was based on the usual composition of leachate (Fe, Cl^-, TOC) and the individual composition of the industrial waste being leached. Due to the preliminary nature of the data, no statistical analysis was attempted. For purposes of this report, an attempt was made to directly compare the limited data available for each test cell. To provide illustrations of these comparisons, the results from the monthly analyses are presented in graphs as cumulative mass releases. In this manner, a preliminary comparison of the leaching data can be made for the untreated, treated, and control test cells.

Leachate Quality from Control Test Cells

Factors influencing leachate quality include degree of compaction of refuse, rate of infiltration, moisture content, composition and processing of waste, and the time over which decay has occurred. Table 6 compares the range of values for leachate analyses from the control (MSW only) test cells in this study to those summarized by

TABLE 6. COMPOSITION OF LEACHATES FROM CONTROL TEST CELLS

Parameter*	Control Test Cells in This Study	Chian and DeWalle†	James
Age (months)	8-17	12-193	24-240
COD	325,400-76,300	40-89,520	79-30,933
BOD	13,000-25,500	81-33,600	--
TOC	7,000-12,000	256-2,800	--
pH	4.35-5.55	3.7-8.5	--
TVA	38-12,000	--	--
Specific Conductance	6,000-9,800	2,810-16,800	2,050-13,500
Alkalinity	1,750-3,820	0-20,850	--
TKN	711-902	0-1,106 (NH_3)	--
TP	13.6-39.2	0-130	--
Cl	867-1442	4.7-2,467	--
F	<0.01-2.12	--	--
Al	1.69-6.08	--	--
As	<.001-0.045	--	--
B	6.00-8.38	--	--
Be	<.005	--	--
Ca	655-1,118	60-7,200	--
Cd	0.004-0.028	0.03-17	0.001-0.073
Cr	0.089-0.338	--	0.01-0.29
Cu	0.004-0.030	0-9.9	0.004-1.54
Fe	229-362	0-2820	6.5-1,500
Pb	<0.001-0.082	<0.1-2.0	0.01-0.33
Mg	138-178	17-15,600	--
Mn	11.0-18.6	0.09-125	--
Na	712-942	60-7,700	--
Ni	0.268-0.482	--	--
K	357-615	28-3,770	--
Se	0.078-0.160	--	0.001-0.33
Zn	6.75-21.7	0-370	0.07-33.0
Hg	<0.0002-0.0030	--	0.0006-0.16
ORP†	(-450)-(-73)	(-220)-(+163)	--

* All values in mg/ℓ except specific conductance which is measured as micromhos per centimeter, pH in Ph units, and ORP in millivolts.

† 23 leachates analyzed by Chian and DeWalle.

Chian and DeWalle[11] and to those listed by James[12]. The ranges of analytical results from the control test cells are consistently within the previously reported ranges for all constituents.

The leachate analyses reported in this paper were obtained from simulated landfill test cells during the period from 8 to 17 months after sealing. The leachate samples are representative of young landfills. The highest concentrations for BOD, COD, TOC, TVA, and alkalinity were measured in the first and second quarterly samples. These data are typical for young landfill leachates as reported by other investigators[11,12].

Metal concentrations (with the exception of zinc, lead, and beryllium), ORP, and specific conductance have all tended to fluctuate randomly. Zinc and lead concentrations have declined from initial high values (Table 6) to near the lower limit of the reported zinc and lead concentration ranges. To date, Beryllium has not been present in detectable amounts in any of the control test cell leachates.

Cumulative Mass Releases of Contaminants

Comparisons of the cumulative mass of contaminants leached from the various test cells are based on data normalized to the weight of MSW in the test cell. Increases in the total mass of contaminant leached per unit weight of MSW from the co-disposal test cells over that leached from the controls can be assummed to be due to release of contaminants from the material co-disposed with the MSW. Graphs comparing the total masses of leached contaminant per kilogram of MSW for the untreated and treated co-disposal test cells and the controls are presented as Figures 4 through 11. The plots for the controls are average values for the two control test cells. Plots for the treated sludges were developed for Process A only due to the limited data available for Process B treated sludges. Table 7 and 8 show the cumulative mass releases for the parameters measured on a monthly and on a quarterly basis, respectively. Plots of pH for various leachates are presented as Figure 12.

Electroplating Waste (Sludge 200) -

Of the 17 metals analyzed for the test cell containing untreated sludge 200 and MSW, boron, calcium, magnesium, nickel, and sodium, have mass releases above control cell levels. Releases of chromium and copper, which are characteristic of Sludge 200, were not detected in concentrations above the control cell releases. The cumulative mass releases of boron, copper, nickel, potassium, selenium, and zinc for the chemically stabilized Sludge 200 were greater than those released by the control cells (Table 8). The pattern of cumulative release of TOC (Figure 7) and other demand parameters (Table 8) indicates that neither the co-disposal of untreated or treated Sludge 200 significantly alters the character of the MSW leachate. Also, little difference was observed in the pH of the untreated and treated Sludge 200 when compared with the controls (Figure 12).

Chlorine Production Brine Waste (Sludge 800) -

Numerous metals, including As, Al, Ca, Cd, Cu, Hg, K, Mg, Mn, Ni, Na, Pb, and Zn have been leached from untreated Sludge 800 in appreciable quantities above those found for the control cells.

As anticipated, significant quantities of Cl have also been leached from the untreated sludge (Figure 5). Figures 8 and 9 show the mass releases of Cd and Hg, respectively. The only metal from untreated Sludge 800 showing no measurable increase over the control test cells is iron.

The relative effectiveness of chemical stabilization on Sludge 800 (compared to the untreated and control test cells) is shown in Figures 5, 8, 9, and 10. The mass leaching of toxic metals such as Cd, Hg, and Cr have been significantly reduced. The only cumulative mass releases of metals still above the control test cells after chemical stabilization are for Ca, K, and Na.

Little difference has been observed in the leaching of TP, TKN, COD, BOD, TVA (Table 8), and TOC (Figure 7) between the Sludge 800 co-disposal cells and the control cells. The pH of the untreated, treated and control cell leachates have been virtually the same during the initial 9 months of leachate production (Figure 12).

Calcium Fluoride/Sewage Waste (Sludge 900)-

Cumulative mass releases of Cd, Cu, Mg, Mn, and Se higher than the control test

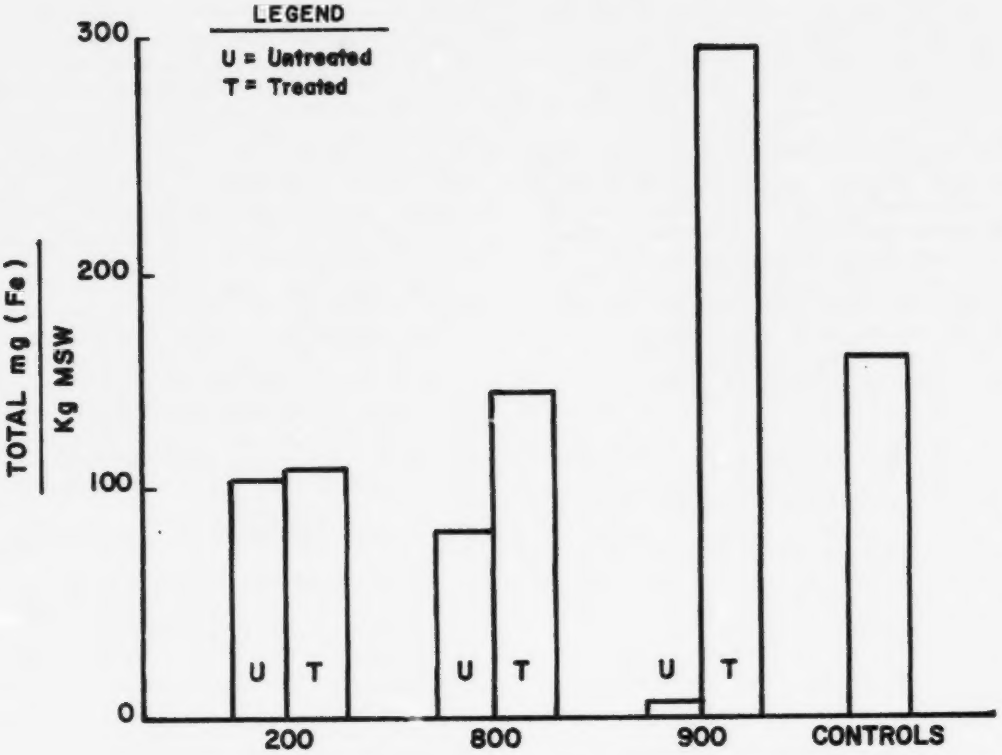

Figure 4. Cumulative mass release of Iron.

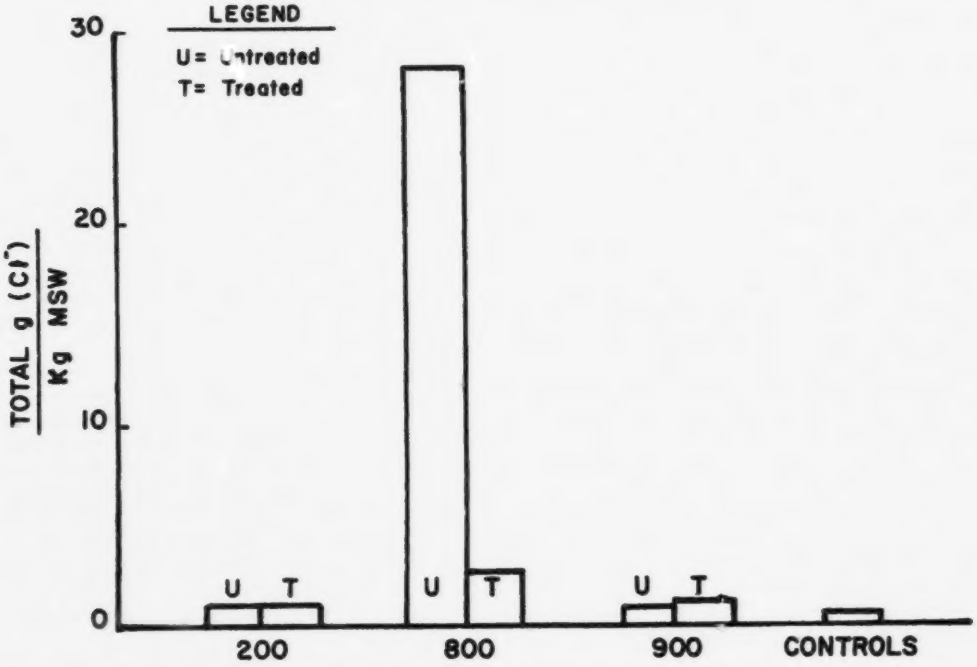

Figure 5. Cumulative mass release of Chloride.

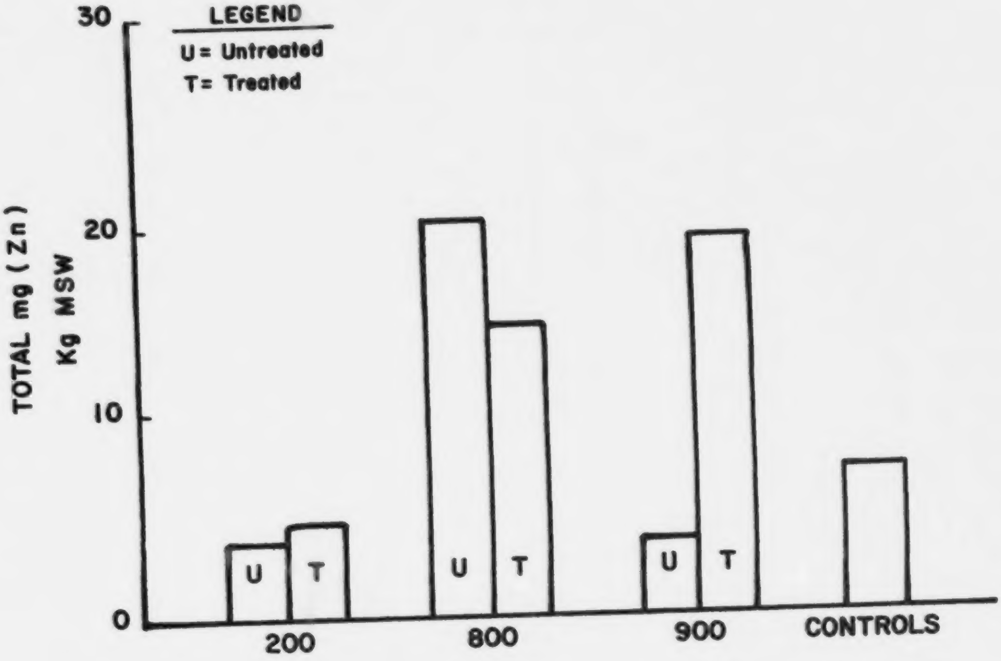

Figure 6. Cumulative mass release of Zinc.

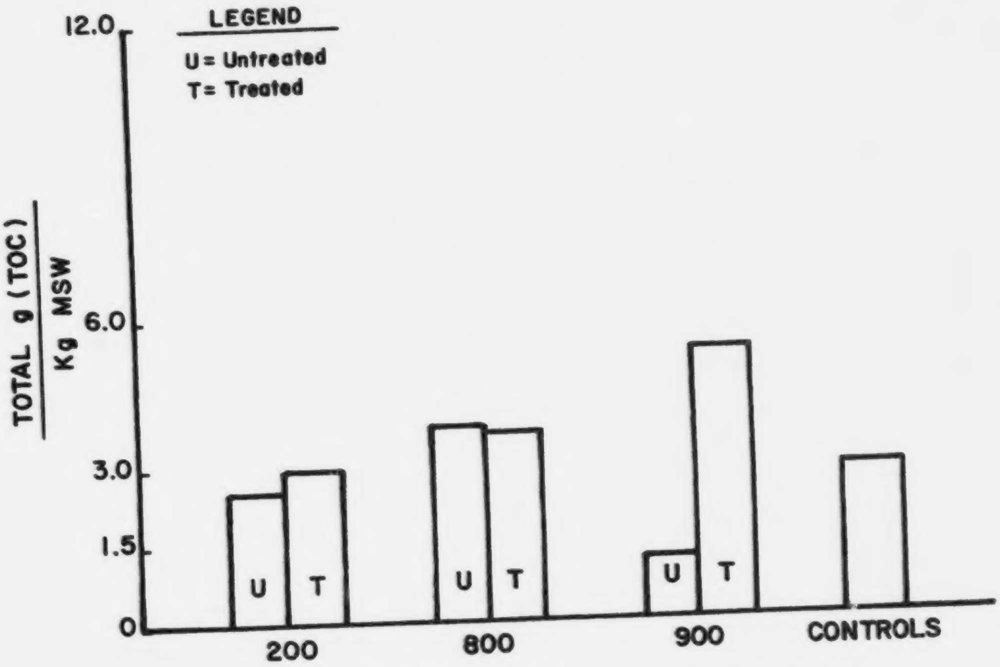

Figure 7. Cumulative mass release of Total Organic Carbon.

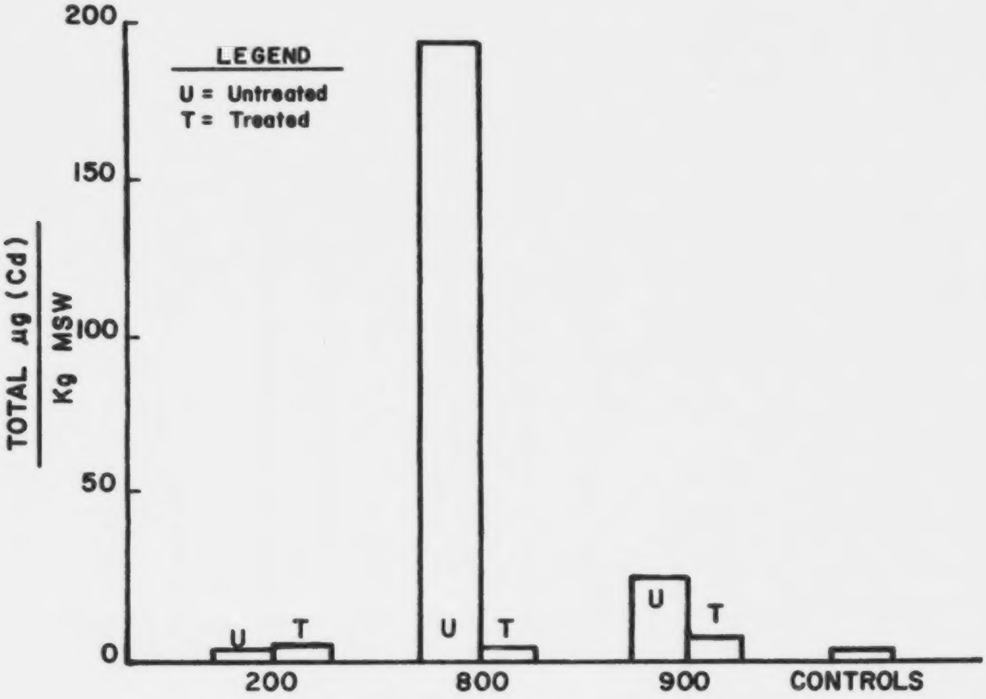

Figure 8. Cumulative mass release of Cadmium.

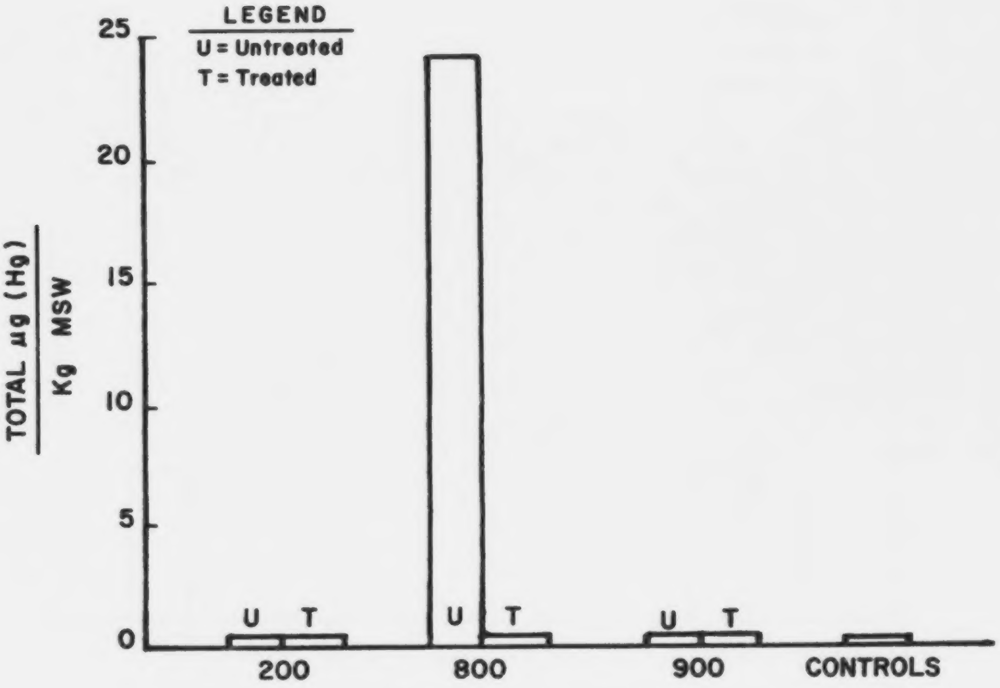

Figure 9. Cumulative mass release of Mercury.

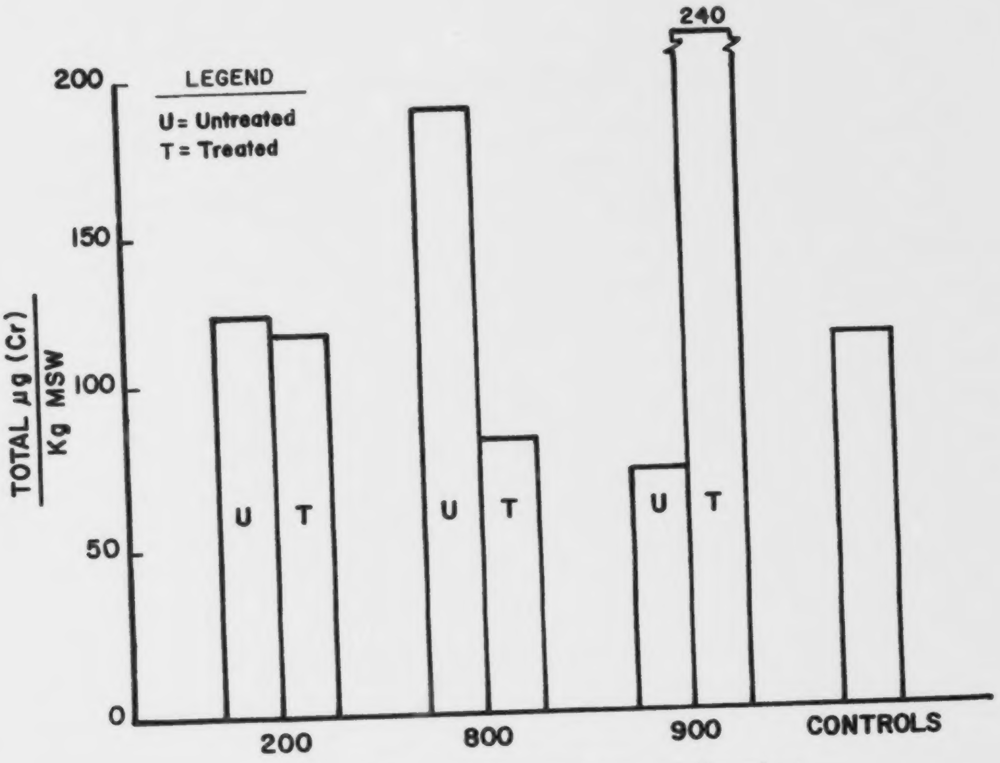

Figure 10. Cumulative mass release of Chromium.

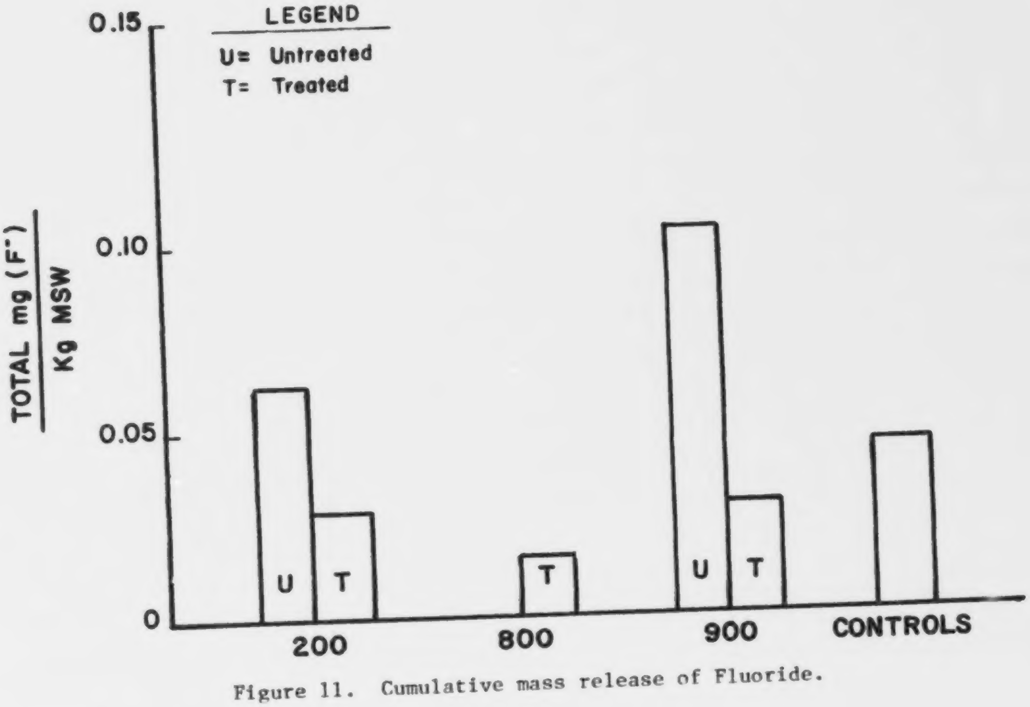

Figure 11. Cumulative mass release of Fluoride.

TABLE 7. CUMMULATIVE MASSES LEACHED PER KG MSW
(MONTHLY PARAMETERS)

Parameter	Controls	Sludge 200 Untreated	Sludge 200 Treated	Sludge 800 Untreated	Sludge 800 Treated	Sludge 900 Untreated	Sludge 900 Treated
Alkalinity (mg)	1.14	1.53	1.66	1.50	1.65	1.73	4.08
Chloride (g)	0.490	0.587	0.605	30.11	0.284	0.533	1.30
TOC (mg)	29.3	24.9	31.1	38.1	36.6	11.6	51.3
Cd (μg)	3.94	3.63	4.19	199	7.11	24.7	7.25
Cr (μg)	119	130	120	193	86	75	240
Hg (mg	0.6	0.4	0.4	21.7	0.4	0.4	0.7
Fe (mg)	147	100	101	78	138	4	296
Zn (mg)	6.8	3.9	14.5	21.1	5.1	3.7	19.2

TABLE 8. CUMULATIVE MASSES LEACHED PER KG MSW
(QUARTERLY PARAMETERS)

Parameter	Controls	Sludge 200 Untreated	Sludge 200 Treated	Sludge 800 Untreated	Sludge 800 Treated	Sludge 900 Untreated	Sludge 900 Treated
Al (mg)	1.13	0.906	0.525	15.1	0.824	0.848	0.971
As (μg)	8.25	<12.0	<11.0	55.5	<12.0	<8.8	12.3
B (mg)	2.8	10.33	5.43	5.18	3.97	4.54	8.69
Be (μg)	<10.0	<6.0	<6.0	<7.0	<11.0	<8.0	<17.0
Ca (mg)	301.0	743.0	454.0	751.0	493.0	370.0	870
Cu (μg)	6.3	5.65	12.9	106.0	6.14	25.0	9.17
Pb (μg)	7.51	2.26	4.64	88.5	4.17	<0.88	4.99
Mg (mg)	71.1	163.0	90.1	235.0	83.6	142.0	177
Mn (mg)	6.86	7.78	6.92	12.94	8.15	15.0	14.59
Ni (μg)	174.0	263.0	266.0	490.0	192.0	122.0	340
K (mg)	251.0	290.0	424.0	512.0	416.0	242.0	734
Se (μg)	49.3	35.7	87.1	106.0	71.4	71.9	66.3
Na (mg)	400.0	673.0	536.0	2130.0	1810.0	213	944
TP (mg)	9.4	4.1	8.79	8.01	11.08	4.24	17.29
TKN (mg)	381.0	346.0	681.0	495.0	406.0	309.0	885
BOD (kg)	9.33	8.97	7.92	10.88	8.53	5.59	21.54
TVA (g)	1.88	1.49	1.59	1.23	1.15	1.10	1.94
COD (kg)	14.90	15.60	17.93	19.20	15.24	10.12	29.90
F^- (μg)	75	61	26	<20	14	102	30

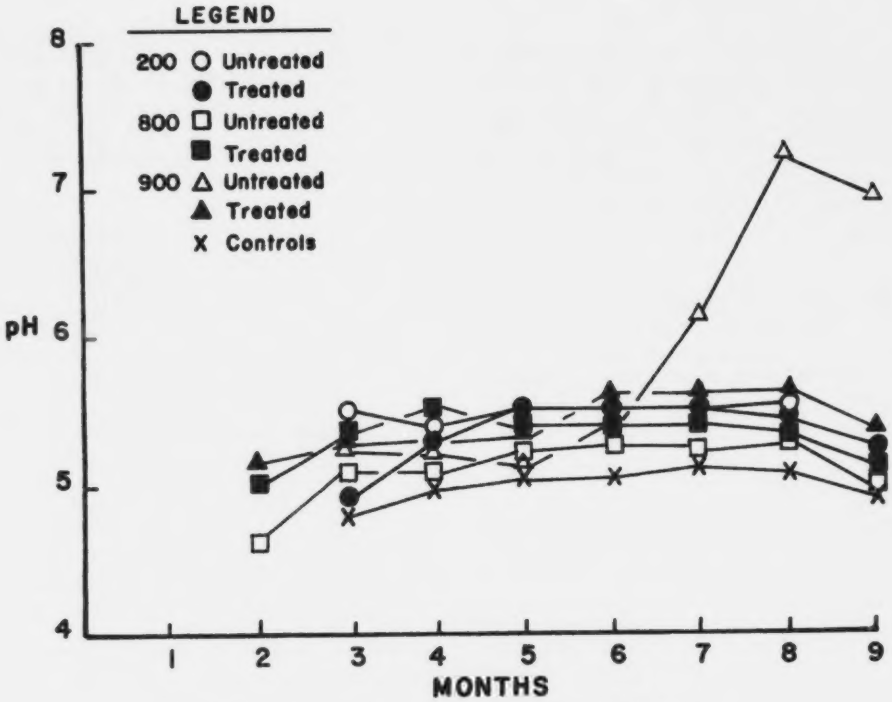

Figure 12. Variation in leachate pH values.

cells have been observed for the untreated Sludge 900 co-disposal test cell. Leaching of Na and Fe have been noticably lower than the control cell values. The remaining 10 metals have been leached at approximately the same levels as that for the control test cells. The chemically stabilized or treated Sludge 900 co-disposal cells have shown a cumulative release of B, Ca, Cr, K, Mg, Mn, Ni, and Zn above the control cells. These cumulative mass releases are probably related to an unexplainable increase in leachate production from the test cells containing the treated Sludge 900. Beginning 5 months after the initiation of leachate production, leachate quantities increased dramatically to an amount almost equivalent to the amount of infiltrate applied. Checks are being made to ascertain whether the test cells have received more water than originally scheduled or if there exists an anomally in the leaching characteristics of the test cells. Figure 11 shows the cumulative fluoride leached from the treated waste test cells. Cumulative mass releases for both the untreated and treated Sludge 900 co-disposal cells were higher than for the control cells. Actual concentrations of fluoride released have been less than 3 mg/ℓ. Chloride levels released from the treated waste are near the control levels (Figure 5).

TOC (Figure 7) and other demand parameters (Table 8) for the untreated Sludge 900 have been considerably less than that shown for the controls; whereas, the same parameters from the treated sludge co-disposal cells have been at or above the control levels.

The pH of the leachate from the untreated Sludge 900 has risen from 5.0 to 7.2 (Figure 12). The significant rise in pH and concurrent reduction in demand parameters tend to indicate an accelerated rate of stabilization of test cell contents, perhaps due to overwatering of the cells or to the availability of the organics from the sewage sludge.

CONCLUSIONS

Contaminant characteristics of leachate generated from the control test cells in this study are consistent with data reported elsewhere.

Release of the major metal contaminants

of electroplating sludge when co-disposed with MSW was not observed.

Untreated chlorine production brine sludge when co-disposed with MSW, releases significant quantities of Al, Cd, Cu, Cl, Hg, Na, and other dissolved solids. Chemically stabilized chlorine production brine sludge when co-disposed with MSW significantly reduces the mass release of toxic metals (e.g. Cd, Hg, and Cr) as well as chlorides.

To date the co-disposal of industrial wastes with MSW has not significantly affected the traditional leachate pollution indicies of BOD, COD, TOC, alkalinity, pH, and iron with the exception of the untreated calcium fluoride/sewage sludge.

ACKNOWLEDGMENTS

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STABILIZATION AT MUNICIPAL LANDFILLS CONTAINING INDUSTRIAL WASTES

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ABSTRACT

The technical feasibility and merit of codisposal of municipal and industrial wastes in landfills are discussed with specific emphasis on the fate of heavy metals under the influence of leachate containment, collection and recycle. The results of both pilot-scale and lysimeter-type landfill investigations are utilized to describe prominent biochemical and physical-chemical phenomena within the landfill environment, to illustrate probable reaction mechanisms, to develop a control strategy and to indicate a need for some flexibility in regulations governing landfill management options.

Utilizing residential-type solid wastes alone and in conjunction with a metal plating sludge, data have indicated the possibility for significant reductions in leachate heavy metal concentrations and the key roles of redox potential, pH and sulfides, hydroxides and hydroxy-carbonates in sequestering metals. Present studies are being extended to determine limits of heavy metal loadings that can be sustained during codisposal without deleterious effects on the biochemical processes of stabilization within the landfill, and/or the identity of internally produced or externally added mediators which are capable of minimizing these effects.

INTRODUCTION

The production of leachate at landfills has become a sensitive environmental issue with respect to potential damage to ground and surface water resources. This potential for adverse environmental impact will vary depending on leachate quantity and quality as well as the opportunity of migration through and interaction with the surrounding soil or geologic formation to which the leachate is exposed. Moreover, the nature of the waste deposited and its relative chemical stability collaborate to determine leachate characteristics at any time. Therefore, the amount and quality of leachate produced is not only site specific but time dependent thus voiding attempts to use sweeping generalizations in interpretive analysis of leachate problems.

It is the purpose here to review and discuss some of the phenomena occurring during waste stabilization within landfills as promoted by the influx of moisture and controlled by containment, collection and recycle of leachate. Initial emphasis will be placed on the progress of stabilization of municipal residential-type wastes; this emphasis will then be extended to include considerations for codisposal of residential with industrial-type wastes.

FORMATION AND CHARACTERISTICS OF LEACHATE

Regardless of waste type, leachate will be formed when the liquid holding capacity of the landfill is surpassed. In the case of most municipal landfills, leachate is produced when infiltration from rainfall, surface drainage and/or groundwater intrusion combine with the inherent moisture content of the waste to exhaust its liquid holding capacity. The ramifications of such leaching will differ based primarily upon the type of waste being handled and the location at which it has been deposited.

Leachate from Residential-type Solid Waste

For a residential-type solid waste disposal site exposed to leaching opportunities and operated to permit leachate containment, collection and recycle, it is possible to generate data capable of reflecting changes in leachate quality with time. Such information has been presented for lysimeter experiments[1-4] as well as for larger pilot-scale studies.[4-7] The latter efforts are exemplified by recent studies at the Georgia Institute of Technology employing two large (3-m square by 5.2-m deep) lined cells containing shredded municipal solid wastes manually compacted to a density of 319 kg/m^3. Final compacted depths of solid waste were 2.75m and 2.6m in the open and sealed cells, respectively. Moisture from incident rainfall was allowed to enter the open cell directly; the other cell was sealed to permit gas measurements and thus received an equivalent amount of tap water at each rainfall event. The other construction and operational features of the two landfill cells are illustrated in Figure 1 and the characteristics of the shredded wastes placed in each are included in Table 1.

Preliminary results of these studies have been presented previously[5] and have since been extended to include a total test period of 699 days. During this time, the cells reached field capacity, leachate was collected and recycled, and analyses were performed on both leachate and gas samples. Although some leaching occurred initially in both cells on an intermittent basis due to differential moisture movement and uptake within the solid waste mass, it did not appear regularly until 383 days after the waste had been placed. Therefore, about one year was required to promote continuous leaching from the cells.

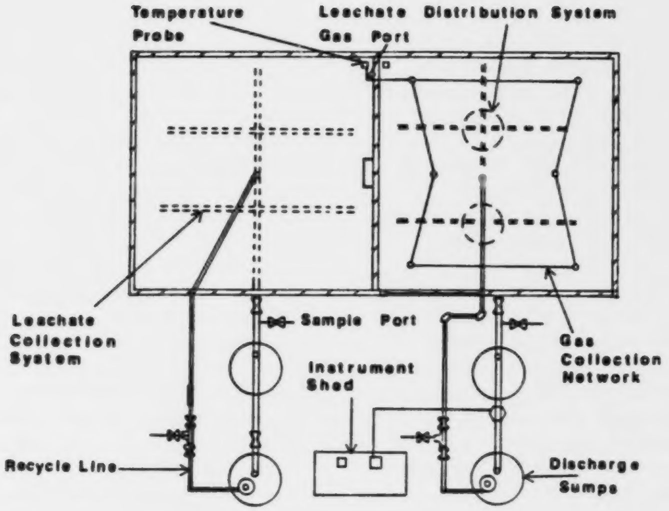
It is informative to compare the leachate analyses at the time when continuous leaching (and recycle) began to those at and after the onset of methane fermentation. The analyses for the open cell for these times are indicated in Table 2 and are considered typical of the longer-term changes to be anticipated in leachate quality at a municipal landfill subject to leaching and having received residential-type solid wastes. In other words, a site will normally accumulate moisture to field capacity, develop an active microbial community, and release leachate commensurate with influx of moisture from rainfall (or groundwater). The leachate initially reflects development of acid fermentation with low pH, high organic content (COD, BOD$_5$, TOC and TVA), a relative abundance of mobilized ions, and obvious pollutional characteristics. Usually by this time, any free oxygen originally present has been depleted, temperatures have stabilized at near ambient and the aqueous environment has become chemically reduced. It is during this period also that some hydrogen will be released in the gas phase, nutrients will begin to be depleted in support of microbial growth and combined oxygen species will serve in the oxidation of complex organic materials to simpler intermediates such as the volatile organic acids. The intensity and/or magnitude of the analytical parameters will vary but the trends will be essentially the same from site to site.

In time, methane fermentation initially restricted to very localized areas, will

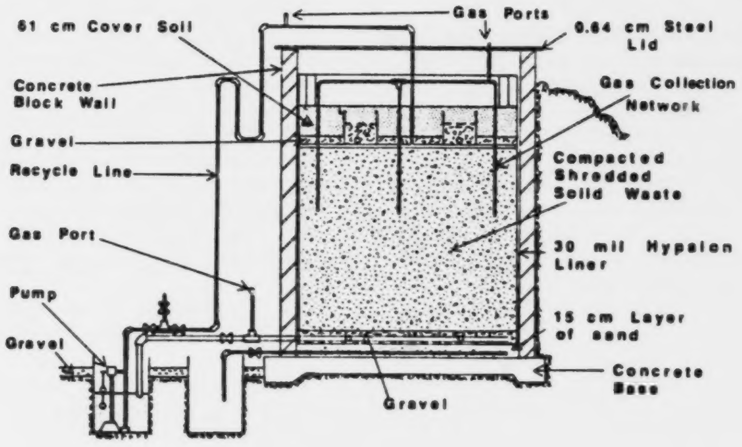
TABLE 1. CHARACTERISTICS OF SHREDDED RESIDENTIAL-TYPE SOLID WASTES USED IN PILOT SCALE INVESTIGATIONS WITH LEACHATE RECYCLE

Parameter	Average Analysis*
Density as placed, kg/m^3	319
Moisture content as placed, %	33.5
Total Volatile Solids, % dry	75.5
Carbon, % dry	45.3
Hydrogen, % dry	5.46
Nitrogen, % dry	3.33
Heating Value, kJ/kg dry	18,045

*Average of six representative samples.


Temperature
Probe
Leachate Distribution System
Gas Port
Leachate
Collection
System
Sample Port
Instrument
Shed
Gas
Collection
Network
Recycle Line
Discharge
Sumps

PLAN OF SIMULATED SANITARY LANDFILLS
(not to scale)


Gas Ports
61 cm Cover Soil
0.64 cm Steel
Lid
Concrete
Block Wall
Gas Collection
Network
Gravel
Recycle Line
Compacted
Shredded
Solid Waste
Gas Port
30 mil Hypalon
Liner
Pump
15 cm Layer
of sand
Gravel
Concrete
Base
Gravel

SECTION VIEW: SEALED CELL (not to scale)

Figure 1. Pilot-Scale Landfill Cells with Leachate Recycle

TABLE 2. CHANGES IN LANDFILL LEACHATE CHARACTERISTICS FROM A RESIDENTIAL-TYPE SOLID WASTE

Leachate Parameter	Leachate Composition		
	Initial*	Intermediate†	Final#
pH	5.3	6.1	6.7
Total Alkalinity, mg/l $CaCO_3$	8,300	4,283	1,338
COD,mg/l	40,210	9,464	350
BOD_5, mg/l	20,437	5,800	88
TOC, mg/l	10,938	2,957	307
Total Volatile Acids(TVA), mg/l HAc	15,611	4,710	ND
Total Kjeldahl Nitrogen, mg/l N	825	374	20
Ammonia Nitrogen, mg/l N	645	111	9
Total Phosphorus, mg/l P	4.93	0.83	0.27
ORP, mv E_c	-	-15	-91
Specific Conductance, μmho/cm	11,850	6,250	1,080
Chloride, mg/l	862	505	178
Sulfate, mg/l	750	110	ND
Calcium, mg/l	2,850	360	260
Magnesium, mg/l	264	153	71
Manganese, mg/l	73.7	1.0	1.6
Sodium, mg/l	1,175	650	515
Potassium, mg/l	1,070	611	311
Iron, mg/l	900	157	39
Zinc, mg/l	2.65	0.1	0.5
Copper, mg/l	ND	ND	ND
Cadmium, mg/l	0.2	ND	ND
Lead, mg/l	ND	ND	ND
Aluminum, mg/l	ND	ND	ND
Chromium, mg/l	0.4	ND	0.3

*After onset of acid fermentation with daily recycle.
†At onset of methane fermentation with daily recycle.
#After methane fermentation with daily recycle.
ND = none detectable.

spread throughout the landfill mass. In conventional landfills, this will be a relatively slow process but with leachate recycle, it will be accelerated due to the benefits of distribution of methane formers and nutrients throughout the landfill mass. Action of the methane formers will deplete methane precursors such as the volatile acids and hydrogen and will increase the quantity of methane gas produced. Reduction in volatile acids will also promote an increase in pH and an opportunity for reactions beneficial to the immobilization of certain ions. Finally, organic pollutant characteristics will be essentially eliminated, the pH will rise to near neutral, and with leachate recycle, opportunities for physical-chemical interactions such as precipitation and filtration on and in the remaining solid waste mass will be enhanced. Ultimate leachate concentrations eventually detected will be a function of dilution and/or opportunity for sustaining continued biological activity within the site.

The fact that anaerobic biological stabilization effectively removes pollutants from leachate is borne out by the changes in parametric composition indicated in both Table 2 and Figure 2. Negative ORP values are indicative of reducing conditions required by anaerobic microorganisms and also are important with respect to feasibility of reduction of oxidized species and enhanced opportunity for interaction, i.e., reduction of sulfates to sulfides and subsequent reaction with metals to cause their precipitation and removal from the leachate. These latter reactions would be of particular advantage in landfills containing potentially toxic heavy metals. The re-

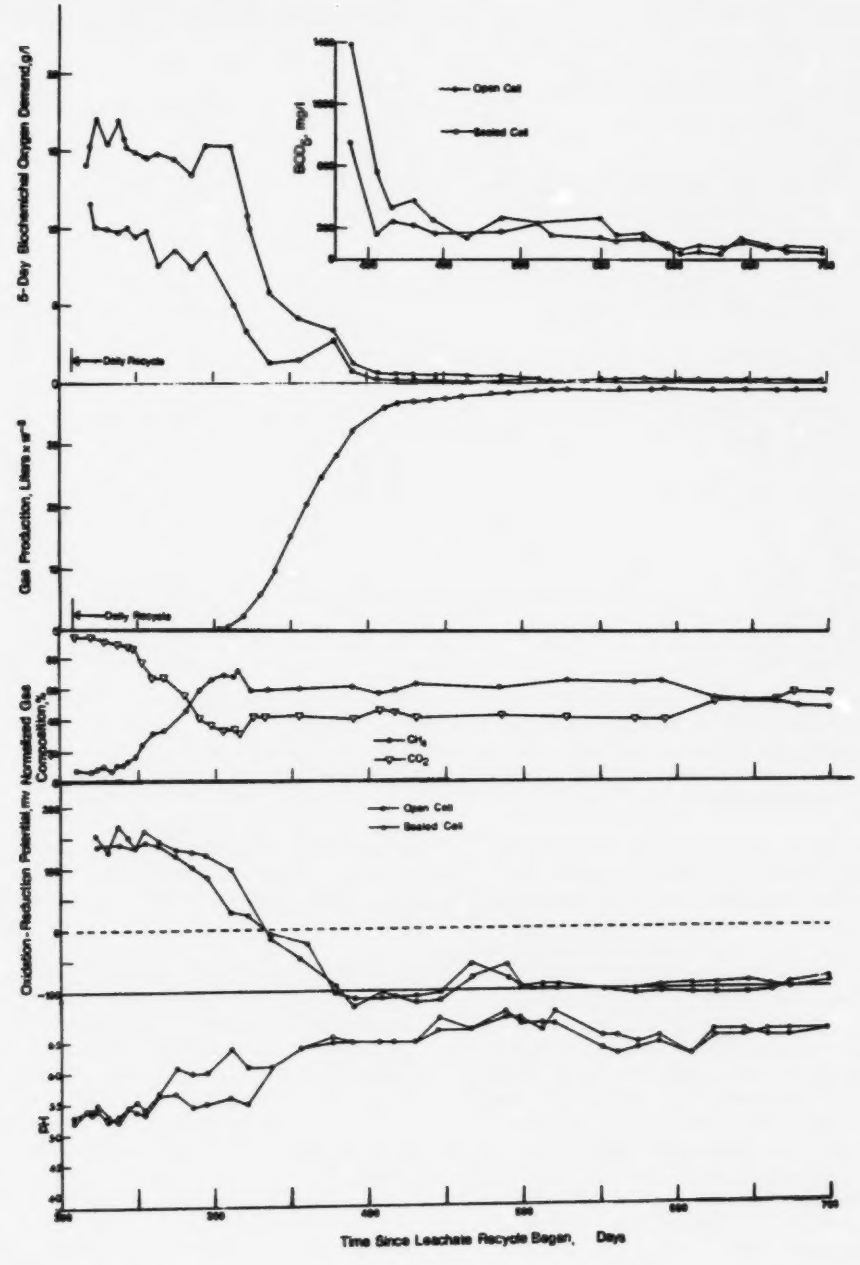


Figure 2. Changes in Leachate Characteristics With Leachate Recycle

duction in the concentration of sulfates, iron and other metals to the low or non-detectable levels indicated in Table 2 could well have been a consequence of such a condition.

Other environmental factors required for support of active biological stabilization of leachate constituents are the availability of substrate and nutrients. Normally, leachate from a recently closed site will contain an abundance of acceptable carbon species; the appearance and subsequent conversion of volatile fatty acids attest to this fact. The overall disappearance of these acids and other organic constituents (measured as BOD_5) with time, coupled with the usual production of methane and carbon dioxide as shown in Figure 2, also support the premise that for residential-type solid wastes, toxicity is not a problem, and that most organic pollutants in leachate are removed by anaerobic biological processes. However, the data in Table 2 would also suggest the possibility of a nutrient deficiency in terms of phosphorus which may have permitted a residual concentration of BOD_5 to linger. This premise tends to be substantiated by the indicated BOD_5:N:P ratios of about 100:10:0.3. Therefore in this case, although nitrogen was in abundance, phosphorus was probably limiting.

Leachate from Residential/Industrial Wastes

Analyses on leachate from the codisposal of residential and industrial wastes will contain in addition to normal leachate constituents, the leachable content of the industrial waste. As a consequence, the industrial waste contribution will act as a superimposition of constituents over and above those normally present without the influence of industrial wastes. The effect will again be highly time dependent and site specific. Therefore, it is difficult to utilize and translate leachate quality data from such sites without prior information on the many variables alluded to heretofore. However, if the constituents and environmental conditions are known, some predictions can be made concerning ultimate impacts.

To demonstrate and provide a basis of discussion of some of the phenomena determining the fate of metal species in landfills, lysimeter studies of the codisposal of residential and industrial solid wastes with leachate recycle have also been initiated at the Georgia Institute of Technology. Four lysimeter columns, used in previous leachate recycle studies[1], have been refurbished to be operationally similar to the units indicated in Figure 3. In this study, residential-type municipal solid wastes were received in bulk, separated into categories, and analyzed for the parameters indicated in Table 3. At the same time, a treatment sludge from the electroplating of zinc and chromium and to a lesser extent, cadmium and nickel was received and analyzed for its metal content as indicated in Table 4. One of the columns served as the control

TABLE 3. CHARACTERISTICS OF BULK RESIDENTIAL-TYPE SOLID WASTES AND SAWDUST USED IN LYSIMETER INVESTIGATIONS WITH INDUSTRIAL WASTE CODISPOSAL AND LEACHATE RECYCLE

Solid Waste Category	Wet Wt., %	Moisture, %	Volatile Solids, %	C, %	H, %	N, %	Heating Value, kJ/kg dry
Paper	53.0	11.6	87.5	41.57	6.76	0.07	15,114
Glass	13.7	-	-	-	-	-	-
Plastic and Leather	8.4	2.5	98.6	82.88	8.89	0.06	37,932
Diapers	2.9	2.1	98.2	46.89	6.04	0.55	20,432
Garden Debris	1.8	0.7	92.4	45.03	5.90	0.09	16,873
Food Wastes	6.2	75.4	92.0	41.76	6.61	1.97	18,966
Wood	2.0	-	-	-	-	-	-
Metals	5.9	-	-	-	-	-	-
Fines	6.1	45.1	90.0	40.65	5.47	0.97	15,282
Sawdust	-	7.6	88.1	43.41	5.94	0.09	17,961

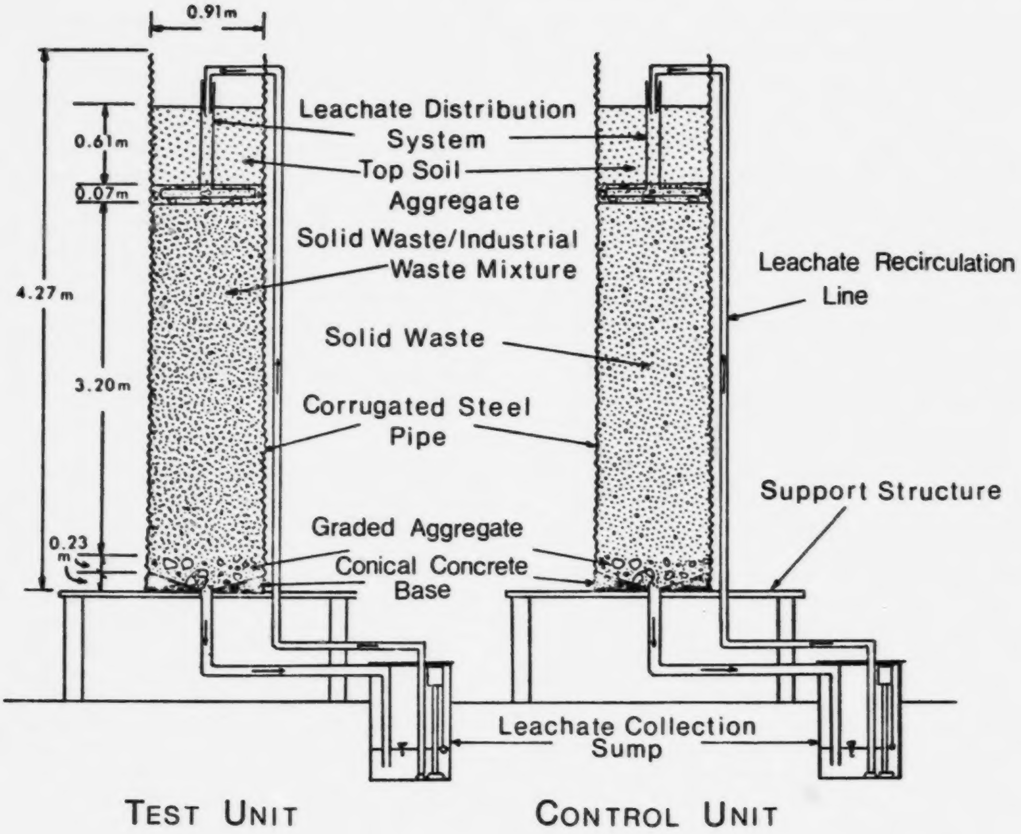

0.91m
4.27 m
0.61m
0.07m
3.20m
0.23 m
Leachate Distribution System
Top Soil
Aggregate
Solid Waste/Industrial Waste Mixture
Leachate Recirculation Line
Solid Waste
Corrugated Steel Pipe
Support Structure
Graded Aggregate
Conical Concrete Base
Leachate Collection Sump
TEST UNIT
CONTROL UNIT

Figure 3. Simulated Landfill Lysimeter Columns with Leachate Recycle

and received 400 kg of bulk residential solid wastes and sawdust without any metal sludge; the other three columns received the same amount of residential solid wastes together with 33.6 kg, 65.8 kg and 135.2 kg of metal sludge, respectively. The solid waste and/or metal sludge in each case was mixed with 37.3 kg of sawdust and placed in successive layers throughout the columns as they were being filled. The columns were then covered with soil, brought to field capacity with tap water and allowed to leach as a consequence of the influx of rainfall and the recycle of leachate back through the columns.

Although the research investigations are continuing, preliminary results have indicated that acid fermentation has set in, that the pH has been lowered, and that certain ionic species have been transferred to the leachate and appear in concentrations indicated in Table 5. Although

TABLE 4. CHARACTERISTICS OF METAL SLUDGE USED IN LYSIMETER INVESTIGATIONS WITH RESIDENTIAL-TYPE SOLID WASTES CODISPOSAL AND LEACHATE RECYCLE

Parameter	Analysis
Moisture Content, %	84.7
Volatile Solids, %	24.6
Zinc, mg/kg dry	317,000
Chromium, mg/kg dry	21,000
Nickel, mg/kg dry	400
Cadmium, mg/kg dry	13,100
Copper, mg/kg dry	185
Iron, mg/kg dry	94,000

Note: Metals determined after acid digestion.

TABLE 5. SELECTED INITIAL LEACHATE CHARACTERISTICS FROM LYSIMETER INVESTIGATIONS OF CODISPOSAL OF RESIDENTIAL-TYPE SOLID WASTES WITH INDUSTRIAL WASTE AND WITH LEACHATE RECYCLE

	Analyses			
Parameter	Column 1	Column 2	Column 3	Column 4
pH	5.68	5.45	6.08	6.17
Alkalinity, mg/l $CaCO_3$	1,010	1,190	1,370	1,980
COD, mg/l	11,740	20,830	13,450	13,830
BOD_5, mg/l	5,900	10,400	6,000	6,200
Total Volatile Acids, mg/l HAc	989	1,320	874	1,220
Suspended Solids, mg/l	114	11	6	18
Dissolved Solids, mg/l	6,510	11,200	7,830	10,180
ORP, mv E_c	-100	-80	-90	-80
Sulfate, mg/l	34	218	104	109
Sulfide, mg/l	1.2	0.03	0.03	0.03
Zinc, mg/l	3	500	205	390
Chromium, mg/l	0.05	0.28	0.20	0.12
Nickel, mg/l	0.10	1.1	0.82	1.2
Cadmium, mg/l	ND	1.7	1.1	2.0
Copper, mg/l	ND	ND	ND	ND
Iron, mg/l	25	88	68	62

Column 1: Control without metal sludge.
Column 2: Test unit with 33.6 kg of metal sludge.
Column 3: Test unit with 65.8 kg of metal sludge.
Column 4: Test unit with 135.2 kg of metal sludge.
ND = Nondetectable.

there was some dissimilarity between some of the initial analyses, probably consequenced by some unavoidable differences in the bulk wastes received by each lysimeter column, some of these variations will likely be moderated by continued recycle operation. Moreover, because of the differing amounts of metal sludge added to the three test columns, some variations in leachate characteristics were anticipated. It is too early in the investigation to speculate on the eventual changes in parametric concentrations caused by the inherent biochemical and physical-chemical processes within each column, but it is anticipated that biologically mediated stabilization will continue at least at the lower metal concentrations with the eventual sequence of events described previously. Accordingly, changes in analytical parameters similar to those indicated in Table 2 should occur; of particular interest will be the eventual fate of the higher metal concentrations with respect to opportunity for removal under the combined invluences of leachate recycle and stabilization.

GENERAL DISCUSSION

The results to date on the present lysimeter studies, augmented by experiences elsehwere, allow some speculation on the fate of metals in landfill leachates during biochemical stabilization. Of particular interest are the pertinent equilibria, the pH and ORP, and the availability of various constituent species for physical-chemical interaction.

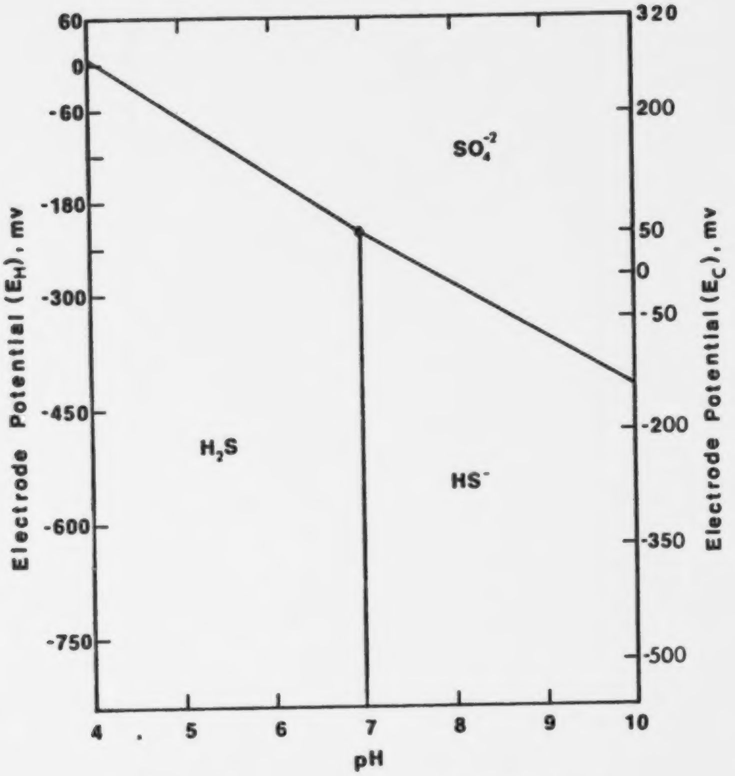
It is known that when the impacts of leachate production are most detrimental, the pH is low, the chemical environment has become reduced and a primary determinant of the presence or absence of various constituents will be their relative solubilities in the leachate medium. In a biochemically reduced environment similar to that indicated in Table 2, certain previously oxidized species will be transformed to their reduced counterparts. For example, nitrates and sulfates will typically be reduced to ammonia and hydrogen sulfide, respectively. These species ionize in accordance with known equilibrium relationships, the former as a weak base, the latter as a weak acid. As such, they contribute to the buffer capacity and help to moderate the pH.

In many landfills, the sulfate-sulfide redox system is of additional importance because of the role it has to play in the eventual reaction with and removal of metals. Typically, when leachate pH and ORP are low, sulfates will have been reduced to sulfides and the fate of many metals will be determined by relative concentrations and the solubilities of the metal sulfide products.

Figure 4 demonstrates the anticipated distribution of SO_4^{-2}- S^{-2} species as determined by ORP ($E_H = E_c - 282mv$) and pH[9]. The boundary limits for each region of the figure represent loci of equimolar concentration of the two indicated species separated by the respective boundaries. It is important to note that, since the reduction of sulfate to sulfide requires eight electrons per mole, a change of as little as 12mv toward reducing potentials will cause a 10-fold increase in the ratio of sulfide to sulfate species. Moreover, since heavy metal sulfides tend to be so sparingly soluble, even at acid pH values where HS^- or H_2S predominate, sufficient S^{-2} will be present in equilibrium with the HS^- and H_2S to encourage precipitation of most metals. Finally, as S^{-2} is removed by precipitation, the sulfide equilibrium will shift in accordance with Le Chatelier's principle, to generate more S^{-2}. In effect, therefore, a very high percent of the total $[H_2S] + [HS^-] + [S^{-2}]$ is available for precipitation of metal sulfides.

Given that sulfate is present and that complete reduction to sulfide has occurred within the landfill environment, the immobilization of specific metal constituents will then be controlled by the relative solubilities of the respective sulfide species. For the studies under consideration, Figure 5 indicates the exceedingly low concentrations of heavy metals (Zn^{+2}, Pb^{+2}, Cd^{+2}, Cu^{+2} and Cr^{+3}) to be anticipated upon reaction with sulfides (0.02 moles/liter) throughout the broad pH range of 3 to 11. Under the reducing conditions observed in the experimental studies but with an increasing pH consequenced by the conversion of volatile acids to methane in a biochemically active landfill, these solubility profiles progressively become even lower.

In addition to the preceding, those metal species that are inevitably present and/or exist in several oxidation states deserve special consideration. Iron (and manganese) is a normal ingredient of landfill leachates and would exist in the reduced Fe^{+2} form. It would also be precipitated as sulfide under the stated conditions but somewhat less favorably than the other indicated metals (In contrast, mercury would exist as Hg_2^{+2} but would be highly insoluble as Hg_2S.) On the other hand, chromium would be reduced to Cr^{+3} but at redox potentials (E_H) approximating -400mv, a transition occurs from the trivalent to the divalent state. Available solubility data suggest that sulfides would play no role in the removal of chromium in either state and that solubility will depend upon hydroxide



$$SO_4^{-2} + 9H^+ + 8e^- \longrightarrow HS^- + 4H_2O \qquad \log K = 34$$

$$SO_4^{-2} + 10H^+ + 8e^- \longrightarrow H_2S + 4H_2O \qquad \log K = 41$$

$$HS^- + H^+ \longrightarrow H_2S \qquad \log K = 7$$

Figure 4. Species Distribution Diagram for Sulfate-Sulfide Equilibrium as a Function of pH and Electrode Potential

equilibrium. In this regard, Cr^{+3} is much less soluble than Cr^{+2} ranging from 200 mg/l at a pH of 5 to 100 µg/l at pH 7 as compared to 100 mg/l at pH 7 for the divalent state. Therefore, chromium would tend to be one of the most mobile of the heavy metals in landfill leachates.

In those rare cases where sulfide concentrations are very low or have been depleted due to their removal or the possible reinstatement of oxidizing conditions, the fate of the metals becomes considerably more complex. With sulfide concentrations as low as 10^{-6} molar, the removal of zinc would no longer be controlled by sulfide and would, like chromium, depend upon hydroxide equilibria. However, superimposed on this reaction opportunity would also be the relative influence of the carbonate-bicarbonate equilibrium which would in the absence of sulfide, help determine the probable precipitating species. For instance, assuming an alkalinity as $CaCO_3$ of 2000 mg/l and a pH of 6.5 in the absence of sulfides,

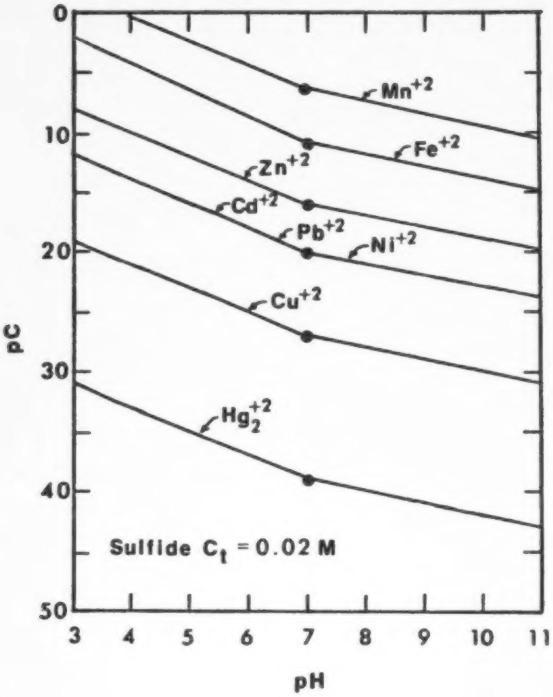


Figure 5. Solubility Profiles for Selected Metals as a Function of pH and Sulfide Concentration

the probable precipitate species would be $CdCO_3$, $Cu_3(CO_3)_2(OH)_2$, $PbCO_3$ and $Cr(OH)_3$; zinc and nickel would be least likely to precipitate, probably as respective carbonate and hydroxy-carbonate species if at all and would therefore be most mobile under the indicated conditions. However, even at equilibrium concentrations of dissolved sulfide as low as 10^{-8} molar, the control of solubility of such metals as Hg_2^{+2}, Cu^{+2}, Cd^{+2}, Pb^{+2} and Ni^{+2} will remain unequivocally in the domain of the sulfide system.

SUMMARY AND CONCLUSIONS

In view of the opportunity for significant attenuation and reduction of contaminant concentrations in leachate from landfills receiving both municipal and industrial wastes, it is possible that rigid and ultrarestrictive regulations on landfilling of such wastes may not be completely justified. This appears to be particularly true of heavy metals when codisposed of with municipal wastes in a controlled manner and with the benefits of leachate containment, collection and recycle.

Whether or not metals will be available for migration from a landfill depends upon their relative concentrations, the state of the chemical environment, and presence of certain companion materials for physical-chemical interaction. The pH and reducing nature of most landfill environments determine the redox couples that predominate and, in the case of heavy metals, emphasize the importance of sulfides in the overall attenuating process. With such a perspective, it is possible to predict probable reaction mechanisms as well as those processes which will be most significant for the ultimate removal of contaminants from the leachate medium. Therefore, with operational control over the leachate, metals precipitated as sulfides (or hydroxides, carbonates, or hydroxy-carbonates) will be further removed with leachate recycle by filtration and/or sorption within the landfill mass.

What remains to be determined for such a landfill management option are the metal loadings which can be sustained without deleterious effects on the biochemical processes responsible for the overall stabilization processes within the landfill and how such effects can be minimized with either restrictions on loading or judicious selection and/or addition of an appropriate sequestering agent. The fact that there are relatively few documented cases of groundwater contamination with heavy metals, even at landfills operated with them for long periods of time, lends credence to such an approach to controlled codisposal of municipal and selected industrial wastes.

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OPTIMIZATION OF LAND CULTIVATION PARAMETERS

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ABSTRACT

Preliminary studies of the effects of amending soils with API oil-water separator sludge on the germination and yield of ryegrass were initiated to generate data on acceptable sludge loading rates and to elicit mechanisms which affect plant responses.

A petrochemical and refinery waste were utilized and each waste was mixed with each of four soils in varying ratios by volume. The mixtures were planted with ryegrass (*Lolium multiflorum*) and emergence and dry matter yields were determined. Eight plant harvest cycles were completed over a 17 month test period. Soil wettability was also determined periodically.

Concentrations of petroleum hydrocarbons as low as 2% v/v depressed ryegrass emergence and yields, apparently through at least two mechanisms. Phytotoxic waste constituents initially acted to severely diminish plant response. Long term yield reductions largely resulted from impaired water, air and nutrient relations associated with recalcitrant hydrophobic hydrocarbons.

The petrochemical sludge suppressed the emergence and yield over a longer period of time. The suppression was proportional to the amount of each waste applied.

INTRODUCTION

Disposal of industrial wastes is a chronic problem intensified by the current awareness of the need for environmentally sound management practices. Of particular importance is the proper handling of potentially hazardous materials which are by-products of the petroleum industry. An effective method of disposal should immobilize, degrade, or isolate the waste compounds such that the possibility for environmental contamination is minimized or eliminated.

Landspreading, also called landfarming, land treatment, and soil incorporation, is the controlled disposal of wastes in the surface soil accompanied by the continued monitoring and management of the disposal site. Although this means of disposal has been used by the petroleum industry to dispose of process sludges, information is still needed on site selection, optimum soil and climatic conditions, application rates and scheduling, decomposition products, potential contaminant emissions and the persistence of toxic residues.

The aims of this research were part of a comprehensive study of the land application of petrochemical sludges. Greenhouse studies were utilized to observe the effects of sludge amendments on the emergence and yield of ryegrass in order to assess the residual toxicity of the wastes as a guide to optimum loading rates.

MATERIALS AND METHODS

SOIL PROPERTIES

Soils of varied properties including mineralogy, texture, organic matter content and reaction were employed to represent a range of potential disposal sites. The four soils chosen were Bastrop, a fine-loamy mixed, thermic Udic Paleustalfs; Lakeland, a siliceous, acid, thermic, coated Typic Quartzipsamments; Nacogdoches, a fine kaolinitic, thermic, Rhodic Paleudalfs and Norwood, a fine, silty, mixed (calcareous) thermic, Typic Udifluvents. The textures of the four soils were sandy clay loam, sandy loam, clay and sandy clay for the Bastrop, Lakeland, Nacogdoches and Norwood soils respectively. The bulk densities were 1.49, 1.38, 1.4 and 1.44 g cm^{-3} at field capacity for each of the four soils respectively. The cation exchange capacity of the soils were 27.4, 0.3, 17.2 and 19.6 respectively. The pH of each soil was 6.86, 6.45, 5.59 and 7.69 respectively.

WASTE CHARACTERIZATION

The waste materials were API oil-water separator sludges from the petroleum industry. A survey of refiners revealed that this class of waste could vary widely depending upon crude stocks, refinery end products, and plant equipment and management. The sludges used in this study were obtained from a refinery producing primarily fuels and lubricants and from a petrochemical plant. Water contents determined by distillation were 41.1% and 20.0% for the refinery and petrochemical wastes respectively. The solvent extractables were quantified gravimetrically following Soxhlet extraction with pentane, benzene and dichloromethane and were 3.09, 3.29 and 3.23% respectively for the refinery waste and 19.75, 13.89 and 4.26% respectively for the petrochemical waste. Residues of 49.3 and 42.8% respectively for the refinery and petrochemical wastes were heated to 750°C and ash was weighed. Ash contents of the refinery and petrochemical wastes were 37.8 and 7.65% respectively. Total sulfur was ascertained by an idometric titration of SO_2 after oxidative combustion and yielded 0.88 and 0.39% S for the refinery and petrochemical wastes respectively. Total N was found by Nesslerization following ammonification of all N sources with a $H_2SO_4:K_2SO_4$: mercuric oxide solution and yielded 0.09 and 0.11% N respectively. Wet combustion with potassium dichromate and $H_2SO_4:H_3PO_4$ yielded total C contents of 10.0 and 35.0% for the refinery and petrochemical wastes respectively.

PREPARATION OF GREENHOUSE POTS

Pots 15 cm ID x 15 cm deep were filled with soil:sludge mixtures and seeded. Waste loading rates were 0, 5, 10 and 20 percent v/v for each soil, and 2,000 cm^3 of the thoroughly mixed soil:sludge was placed in each pot with three replications per treatment. Soils were uniformly fertilized by applying 1 g of 17-17-17 per pot incorporated into the top 2 to 5 cm. This is equivalent to 650 kg/Ha of the fertilizer. Soils were lightly watered, and 100 ryegrass (*Lolium multiflorum*) seeds were broadcast on the surface. Irrigation water applied to pots was from a rain-water collection system.

SEEDLING EMERGENCE COUNTS

Counts of seed emergence were performed as one indicator of the toxic effects of sludge amendments in soils. Four to 6 days after the planting date, daily counts of seedling emergence were begun and continued until no further increase was apparent. Seedling counts were not made once successive plantings no longer indicated a significant treatment effect on emergence.

HARVESTING

Thirty to forty days after seeding, the plant material was harvested for treatment comparisons of dry matter production. All aerial plant material was removed by clipping the ryegrass at the soil surface. Harvested plants were dried in a 60°C oven and weighed to determine yield per pot. Soils were mixed to simulate cultivation and to arrest further growth activity which could interfere with later yield results. Cultivation also insured adequate aeration in order to foster microbial degradation of the wastes. After drying for a period of two to 4 weeks, all pots were replanted with 100 ryegrass seeds per pot. The yield of all treatments decreased with time, indicating a possible depletion of nutrients. Thus a second fertilizer application was made just after the seventh harvest.

RESULTS AND DISCUSSION

Emergence Comparisons Between Soils

For both wastes, the Bastrop soil manifested the highest germination rates as observed over all planting dates over the range of sludge loads. Differences between the remaining soils were minimal. Since this relationship persisted regardless of sludge application, this appeared to be a function of soil properties.

Loading Rate Comparisons of Emergence

The emergence response to varied sludge loads was dependent upon the waste considered. The refinery waste appeared not to alter or in some cases, possibly enhanced germination (Figure 1). In view of the ryegrass seeds' insensitivity to refinery sludge after the first planting, further emergence counts were performed only on petrochemical waste amended soils.

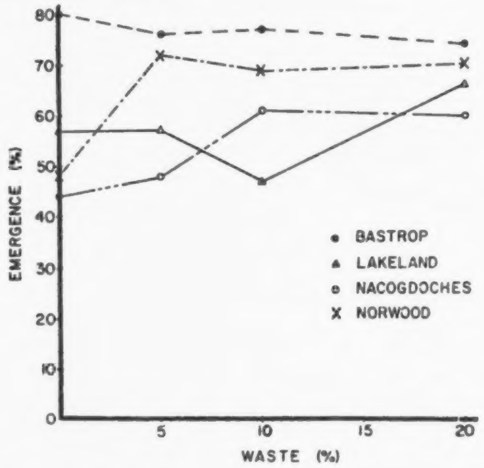

Figure 1. The percent emergence of ryegrass seedlings in four soils treated with refinery sludge.

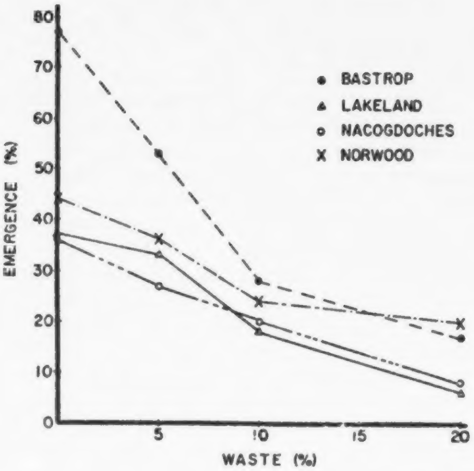

Figure 2. The percent emergence of ryegrass seedlings in four soils treated with petrochemical sludge.

In contrast, petrochemical sludge-amended soils significantly reduced germination in all soils at all three loading rates (Figure 2). Several mechanisms may have operated to inhibit emergence. An increased water repellency was observed when water was applied to sludge-amended soils which may have restricted the water available for seed inbibition.

Another possibly substantial control of emergence could have been the toxic effect of waste constituents. In a review of the effects of plant exposure to oils, Baker (1970) cited several sources which indicated that aromatic compounds, particularly 12-carbon atom aromatics, are highly toxic to plants. Thus, increasing aromatic content could increase toxicity. Aquatic plants, for example, were controlled by as little as 300 ppm light aromatics in water, and foliar applications of oil containing 10% aromatics severely affected maize plants. The aromatics contents of the refinery and petrochemical sludges used in this study were 3.29 and 13.89% (w/w), respectively, which contributed to the soil organics load. The petrochemical plant produces various herbicidal agents as well, residues of which may have been present in the waste.

Changes In Emergence With Time

Successive ryegrass plantings on petrochemical waste-amended soils resulted in increasing emergence, such that after six months the 20% sludge rate evidenced little emergence depression below control plantings. Absorption of water by the soil continued to be poor after six months while the strong sludge odor virtually disappeared after two months. Such qualitative observations suggest that the toxic compounds present in the waste are responsible for depressing emergence. Decomposition and volatilization of phytotoxic compounds could have reduced the concentrations during this period so that seeds on the soil surface no longer suffered adverse effects.

Soil Comparisons of Yields

Corresponding to the emergence results, the yields of ryegrass were found to be consistently highest for the Bastrop soil. Table 1 compares soil effects on yields. Differences were attributable to differences in native fertility and chemical and physical properties, may be another criteria in selecting soils suitable for waste disposal where plant cover is desired.

TABLE 1. SOIL EFFECTS ON RYEGRASS YIELD

Soil	Yield (g/pot) Refinery Waste	Yield (g/pot) Petrochemical Waste
Bastrop	3.45A*	2.33A
Lakeland	2.14 BC	1.20 B
Nacogdoches	2.56 B	1.29 B
Norwood	1.64 C	0.79 B

* Values in a given column followed by the letter do not differ significantly at the 5% level.

Loading Rate Comparisons of Yields

Both the sludges applied effected significant yield reductions below the untreated control. Results from the first harvest where sludges were applied just prior to planting are plotted in Figure 3 and 4. Since the yields for any given sludge rate varied depending upon which waste was applied, concentrations of one or more constituents of the wastes rather than the bulk sludges appeared to regulate plant growth. Comparison of the 20% refinery waste applications to the 5% petrochemical waste treatments suggests the possible influence of total carbon and/or percent aromatics on the yield. The percent carbon reflects the petroleum hydrocarbon content of the soils. Several investigators (Carr, 1919; Plice, 1948; Schwendinger, 1968; Udo and Faymi, 1975) have concluded that oil-associated yield depressions were partially due to impaired aeration and to poor water and nutrient availability. Additionally, as mentioned in the discussion of emergence, aromatics present in the wastes may have been toxic to plants when present in substantial concentrations.

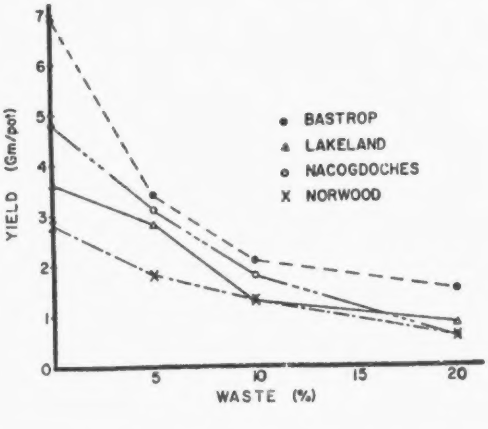

Figure 3. The yield of ryegrass on four soils treated with refinery sludge.

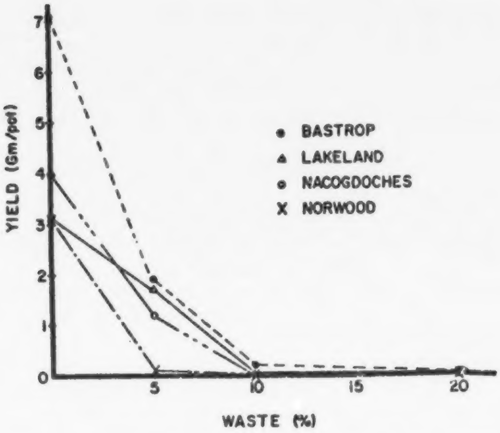

Figure 4. The yield of ryegrass on four soils treated with petrochemical sludge.

Changes In Yield With Time

Degradation of the organic fraction of the API oil-water separator sludges apparently controlled the suitability of sludge-amended soils as a plant growth medium. An initial lag time, characterized by lowered yields, was followed by a period of rapid improvement as toxicity decreased and soil physical relations improved with waste degradation. Apparently, however, recalcitrant oily materials ultimately stabilized yields at levels below control yields, and little further change was noted. After 17 months, ryegrass plants in pots receiving sludge continued to appear sickly and showed symptoms of water and nutrient deficiencies.

Over a 13 month period, yields from refinery waste-amended soils approached control values (Table 2) while the higher rates of petrochemical waste loading continued to reduce yields by 50% or more (Table 3). In a landfarming context, additional petrochemical sludge amendments might increase residual oils in soils to such an extent that plant growth could be depressed even further.

TABLE 2. RELATIVE YIELDS OF RYEGRASS HARVESTED ON TWO DATES FROM REFINERY SLUDGE-AMENDED SOILS

Percent	Relative Yield (% of control)							
	Bastrop		Lakeland		Nacogdoches		Norwood	
	4-26-78	6-4-79	4-26-78	6-4-79	4-26-78	6-4-79	4-26-78	6-4-79
0	100A*	100A	100A	100A	100A	100A	100A	100A
5	49 B	91AB	78AB	80A	64AB	107A	65 B	81A
10	30 C	77 B	35 B	87A	37 BC	78 B	45 C	93A
20	22 C	74 B	23 B	95A	13 C	67 B	22 D	103A

* Values in a given column followed by the same letter do not differ significantly at the 5% level.

TABLE 3. RELATIVE YIELDS OF RYEGRASS HARVESTED ON TWO OCCASIONS FROM PETRO-CHEMICAL SLUDGE-AMENDED SOILS

Percent Waste	Relative Yield (% of Control)							
	Bastrop		Lakeland		Nacogdoches		Norwood	
	4-26-78	6-4-79	4-26-78	6-4-79	4-26-78	6-4-79	4-26-78	6-4-79
0	100A*	100A	100A	100A	100A	100A	100A	100A
5	27 B	87AB	55AB	101A	29 B	104A	2 B	56A
10	3 C	55 B	1 B	97A	1 C	77 B	0 B	44 B
20	0 C	54 B	0 B	60 B	0 C	46 C	0 B	24 B

* Values in a given column followed by the same letter do not differ significantly at the 5% level.

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FIELD VERIFICATION OF LAND CULTIVATION/REFUSE FARMING

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ABSTRACT

Land cultivation practices were observed at six sites disposing of industrial residuals. The sites were selected to permit identification and verification of parameters that contribute to the environmental acceptability of land cultivation for a variety of industrial wastes under markedly different hydrogeological, meteorological and land use conditions. Landfarming at each site investigated was characterized as a physical/chemical/biological waste treatment process. Accordingly, information was obtained on: the physical and chemical composition of the waste fed to the surficial soil treatment system; characteristics of the treatment system; operational procedures; effectiveness of treatment; potential environmental impacts; and costs. To assess the effectiveness of treatment, samples of waste, soil, and waste-soil mixtures were collected and analyzed for organic compound classes; pH; $SO_4^=$ and $C\ell^-$; electrical conductivity; cation exchange capacity; total Kjeldahl nitrogen; As, B, Ca, Cd, Cr, Cu, K, Mg, Mo, Na, Ni, P, Se, V, and Zn. To assess the extent of uptake of inorganic waste constituents, vegetation was collected at most sites and elemental analysis was carried out. Waste inputs to a landfarming system can be characterized quite precisely; output stream can be determined in principle by comparing the composition of waste application areas with the composition of suitably chosen control areas. Treatment processes occurring in the soil system for particular wastes in particular locations can, at the present time, only be inferred from observed compositional changes. This points up the need for long-range research on fundamental mechanisms of waste treatment in soil systems; and short-range research on monitoring protocol for landfarming operations.

INTRODUCTION

Land cultivation/refuse farming is a waste management method that utilizes the natural capacity of soil systems to effect physical, chemical, and biological treatment of certain waste constituents. The practice of land cultivation of municipal sludge is well-established and documented.
Within broad limits, the physical and chemical composition of municipal sludges is relatively constant, and general guidelines can be provided for successful operations. In contrast, land cultivation of industrial sludges is not well documented. Furthermore, the industrial sludges to which land cultivation is potentially applicable include a wide variety of types, compositions and manufacturing sources. Certain oily wastes have been landfarmed, with apparent success, by the petroleum industry for at least 25 years. However, even oily wastes from different sources and at different times can differ significantly in properties that can affect the success of a land cultivation operation.

This paper summarizes observations made at six sites currently landfarming different types of industrial sludges in different areas of the country. The objective of the field work described was to identify and verify parameters that contribute to the environmental acceptability of land cultivation for the management of some industrial residuals. Costs associated with landfarming operations at the sites investigated were also assembled, in order to provide a reference for comparison with costs of other disposal alternatives.

LANDFARMING AS A WASTE TREATMENT METHOD

Landfarming as a waste treatment method is operationally simple and mechanistically complex. Once a site has been established, the basic operations involve essentially: (1) uniform application of wastes to the surface or subsoil of a selected site; (2) cultivation of the applied waste into the soil with a disc or rototiller to assure intimate blending of waste and soil in the zone of incorporation; (3) incorporation of fertilizer, lime or other additives, if necessary, by standard agricultural techniques; (4a) periodic recultivation to assure aerobic conditions in the soil treatment system; (4b) periodic monitoring to determine: the extent of treatment that has occurred; the possible need for pH adjustment; environmental effects; and whether wastes can safely be reapplied; (5) repeat steps (1) through (4b), if no adverse environmental effects have been found, and if re-application is appropriate.

Monitoring (step (4b) above) is of major importance in practical applications, because the rates and routes of action of a given surficial soil treatment system on a particular waste cannot be accurately predicted at this time. The general types of treatment that can occur in the upper soil layers are known. The efficiency and effectiveness of those treatment processes on various components of a complex waste stream are not known. Hence, monitoring is key to assessing the environmental adequacy of the landfarming as a waste treatment method.

Landfarming might be considered among other alternatives for the management of an industrial waste stream, if the following types of treatment, potentially available in soil systems, appear to be applicable without adversely affecting the environment:

- Aerobic microbial decomposition of organic components of the waste -- Wastes which will biodegrade completely and relatively rapidly (say within less than a year) to microbial cell mass, CO_2 and water are particularly good candidates, provided that intermediate products of degradation either do not leach and/or volatilize significantly, or do not adversely impact ground water and/or air if they do migrate.

- Chemical oxidation and/or hydrolysis

- Ion exchange -- binding of cations to unoccupied sites in the soil matrix or substitution of heavy metals in the waste for exchangeable cations (such as Na^+, Ca^{++}, Mg^{++}) in the soil. Once the cation exchange capacity of the soil is saturated, however, the substitution mechanism will release alkali and alkaline earth salts into infiltrating waters.

- Precipitation -- formation within the soil system of relatively insoluble compounds with little potential for migration either via leachate or via biological uptake.

- Neutralization -- In one of the site examples given below, an alkaline lime treatment sludge is used by a turf farmer for neutralization of an acid soil.

While these processes are analogous to those in engineered treatment systems, their mode of action within a soil-waste system is dependent on a far greater range of parameters, and the possibility for side reactions is legion. There is a very extensive literature on the subject. While this paper focusses on waste treatment in surficial soils, landfarming also provides an opportunity for recycling of the components of certain type of wastes. Some wastes can have a beneficial impact on soil structure and soil productivity for plant growth. However, given the complexity of the system, consideration must be given to the potential for unwanted reactions that might impact the environment adversely. In some cases, these might be suppressed by pretreatment of the waste or management of the landfarming system.

STUDY METHODOLOGY

Six sites in different areas of the country were selected for observations of landfarming practices. Field visits were made to each site to document operational practices. Data were obtained, by means of interviews with plant and landfarming personnel, on the origin of the wastes; the character of the sites; the method and rate of waste application; the procedure for mixing wastes into the soil; post waste-addition care; management of the landfarming process; and costs. Samples of waste, soil, and waste/soil mixtures were collected and analyzed for inorganic constituents and organic compound classes in order to provide information for assessing:

- the rate and extent of waste degradation
- the migration of inorganic species, and
- the accumulation of waste constituents in the soil.

Vegetation was collected at most sites and analyzed to assess the extent of uptake of inorganic waste constituents.

Sampling

At each site, samples were taken from 1) the area where waste had been applied and 2) the best identifiable control area. The ideal control area would have been upwind and upgradient of the waste application area, but in all other respects would have been identical to that area except that no waste had been applied. Selection of an appropriate control area was a problem at the majority of sites for a variety of reasons. In general, the design and operation of most sites did not include provision for a bona fide control area as described above. More specifically, problems included substantial variations in soil characteristics, drainage patterns and vegetation occurring within small distances; and uncertainty about the history of waste application outside the boundaries of the present application site. In all cases, a "control" area was selected which necessitated the least compromise in the requirements stated above. In both control and application areas, samples were collected from a 4 x 4 grid covering the area. Wastes were collected from storage facilities or other sources, selected so as to assure that the samples were representative of the waste that was actually applied.

Core samples of soil and soil waste mixture were taken with a sampling tube. The resulting cores were 1" in diameter and 12" in length. These samples were divided in the field into two subsamples corresponding to 0-6" soil depth and 6-12" soil depth. Bulk samples were subsequently coned, quartered and riffled to obtain amounts of sample appropriate for each analysis. Vegetation samples were collected insofar as possible from the same control and application areas from which soil samples were obtained. Unless noted otherwise, composite vegetation samples were prepared from whole plants minus roots. There was no sampling of surface water, runoff, or groundwater at any site during the sampling visits made.

All samples were labeled with codes in the field, so that the identities of participating parties were not apparent from the label information. Analyses of selected soil, soil-waste mixture, and waste samples for Total Kjeldahl Nitrogen (TKN) and Total Organic Carbon (TOC) were performed by Schwartzkopff Microanalytical Laboratories. All other analyses were conducted at Arthur D. Little, Inc. laboratories in Cambridge, Massachusetts.

Analysis Methodology

Inorganic parameters measured included sixteen elements, T.O.C., T.K.N., two anions ($C\ell^-$ and $SO_4^=$), C.E.C., E.C., pH, and DTPA-extractable metals. The methods of analysis are summarized in Table 1.

The organic analysis scheme is shown schematically in Figure 1. The methodology involved:

(1) Solvent extraction with methylene chloride;

(2) Quantitative analysis of volatile and non-volatile organics;

(3) Separation of the extracts by liquid chromatography to divide

TABLE 1. METHODS OF ANALYSIS

Parameter	Method
B, Cu, Cd, Cr, Cu, K, Mg, Mo, Na, Ni, P, Pb, V, Zn	HNO_3-$HClO_4$ digestion, plasma emission spectroscopy
As, Se	Hydride evolution, atomic absorption spectroscopy
Total Organic Carbon (T.O.C.)	Combustion, gravimetric
Total Kjeldahl Nitrogen (T.K.N.)	Digestion, distillation, volumetric
Sulfate	0.1 M LiCl extraction, ion chromatography
Chloride	H_2O extraction, volumetric $Hg(NO_3)_2$ titration
Cation Exchange Capacity (E.C.E.)	Volumetric
Electrical Conductivity (E.C.)	Conductivity meter
pH	pH meter
DTPA-extractable metals	DTPA extraction, plasma emission spectroscopy

the organics into three polarity classes: aliphatic hydrocarbons, aromatic hydrocarbons and polar species; and

(4) Qualitative analysis of organic compound classes present by high resolution mass spectrometry.

The above species, for which analyses were done, accounted for 38-69% of the dry waste weight, depending on the site. Species not determined that might account for the remaining waste weight include Fe, H, O, Si, Aℓ, and non-extractable organics.

OBSERVATIONS

The sites selected for field study represent, by design, a wide diversity of landfarming operations as actually practiced today. None of the sites was established solely for the purpose of obtaining research data. All of the sites serve a significant waste management function. Specific observations at each of the sites, as waste treatment systems, are summarized below.

Site A/Organic Chemical Industry Sludge

Physical and Chemical Composition of Wastes Treated -- The waste being landfarmed at Site A is a secondary wastewater treatment sludge from a batch organic chemicals manufacturing facility (SIC 2865). The waste composition varies significantly over short periods of time, but the volume of wastewater treated is so large that there is some compositional inertia in the sludge generated for land cultivation.

The sludge, as applied, contains about 7% solids and 93% water. Inorganic analysis of the solids fraction yielded the results shown in Table 2. The site is a commercial turf farm, and the waste is being applied primarily for its lime (calcium) content. The waste is also seen to be high in the plant nutrients: potassium, nitrogen and phosphorus. The heavy metals observed in highest concentration were zinc and copper.

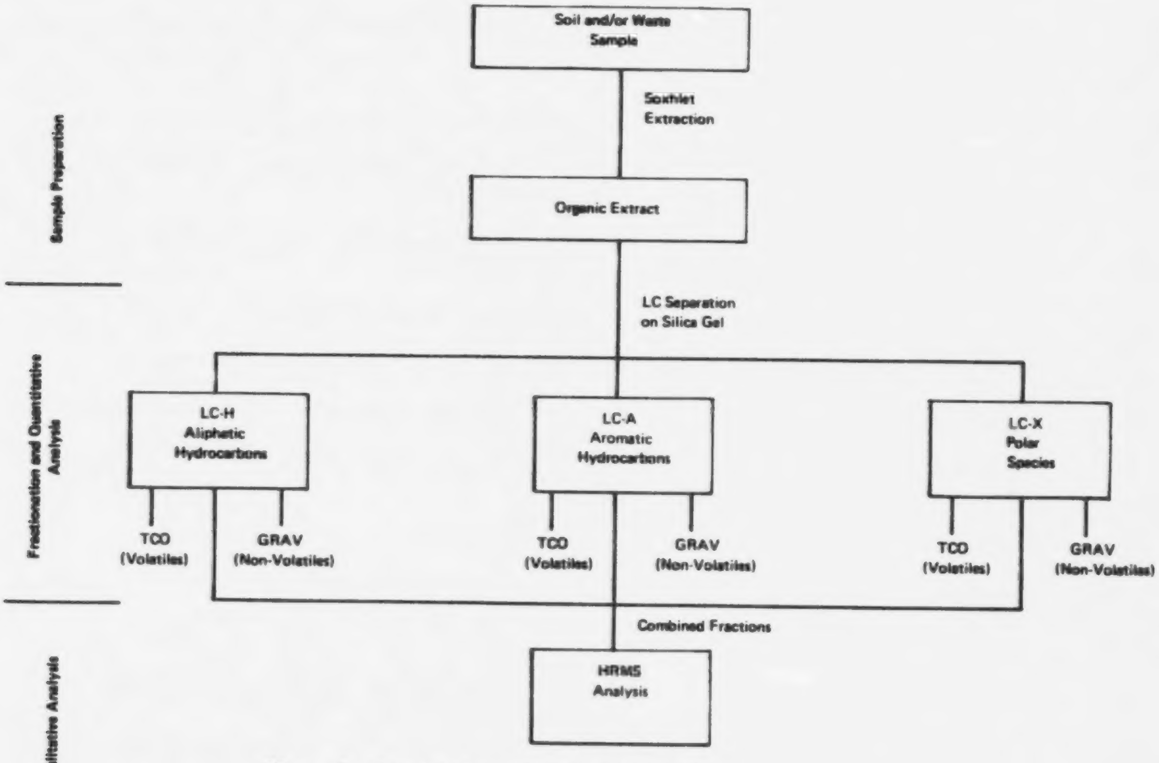
Sample Preparation
Fractionation and Quantitative Analysis
Qualitative Analysis
Soil and/or Waste Sample
Soxhlet Extraction
Organic Extract
LC Separation on Silica Gel
LC-H Aliphatic Hydrocarbons
LC-A Aromatic Hydrocarbons
LC-X Polar Species
TCO (Volatiles)
GRAV (Non-Volatiles)
TCO (Volatiles)
GRAV (Non-Volatiles)
TCO (Volatiles)
GRAV (Non-Volatiles)
Combined Fractions
HRMS Analysis

Figure 1. Flow Chart of Organic Analysis Scheme

TABLE 2. SITE A WASTE ANALYSIS - TOTAL METALS, T.O.C., AND T.K.N.*

Element	As	B	C	Ca	Cd	Cr	Cu	K	Mg	Mo	N	Na	Ni	P	Pb	Se	V	Zn
Concentrations	2	10	16.27%	7.4%	4.8	37	2000	1.8%	4.6%	8.9	2.96%	2%	170	1.7%	100	0.3	17	1900

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* (in µg/g of dried solids, except as noted)

The extractable organics in the waste amounted to 96 mg/L, characterized as follows:

Aliphatic Hydrocarbons, non-volatile (GRAV)	9.5%
Aromatic Hydrocarbons, non-volatile (GRAV)	3.6%
Polar Organics, volatile (TCO)	1.8%
non-volatile (GRAV)	85.0%

The HRMS analysis showed mainly low molecular weight (<150) ions that are probably fragment ions, representing aromatic C, H, N; C, H, O; and C, H, N, O compositions. Since parent ions of higher molecular weight homologs were not found, it seems probable that the actual waste components (from which the fragments are formed) are of sufficiently high molecular weight to be non-volatile at the 300°C probe temperature.

Characteristics of the Site as a Waste Treatment System -- Site A is a turf farm, principally growing bluegrass. The fact that the site supports agronomic activity suggests favorable conditions for biodegradation of waste components amenable to this process. The soil consists of approximately three feet of silt loam underlain by stratified sand and gravel. Waste treatment would be expected to be confined primarily to the relatively shallow surface loams. The cation exchange capacity of the unamended surface soils is in the range of 6.1 - 10.2, which reflects a low to moderate potential for immobilization of heavy metals (such as copper and zinc) by an ion exchange mechanism. However, the unamended soils are also slightly acidic (pH = 5.0 - 5.7), and the increase in pH due to the lime content of the wastes can also increase the cation exchange capacity of the soil. The topography of the site is essentially flat, but drainage is good. Hence, the potential for pooling or flooding, which could create anaerobic conditions, is low. Average annual precipitation is about 40 inches, distributed fairly evenly over the year. This, combined with the high available water capacity in the surface soils, would favor chemical hydrolysis and oxidation reactions for waste components subject to such treatment. Climate is temperate, with mean summer temperatures of 73°F, mean winter temperatures of 29°F, and a frost-free period of about 200 days.

Operational Procedures -- Wastes are transported from an aerated concrete lined lagoon at the plant to the turf farm by tank trucks. Wastes are applied by gravity flow through a nine-foot spreader bar at the rear of the tank truck. The amount of sludge deposited per unit area is a function of truck speed, and is not well controlled. The application area sampled as part of this study was 39 acres in extent. Something of the order of 500,000-2,000,000 gallons of waste had first been applied to the area in 1976, two years prior to our sampling visit.

Following application, the waste is typically allowed to lie on the surface for 1-2 weeks prior to incorporation. Standard farming techniques are used to mix the wastes into the soil. Included are plow harrowing, disc harrowing, reharrowing, dry screening, fertilization and seeding. Once an area is seeded, wastes are not re-applied for 1-1/2 - 2 years, as in the application area sampled in this study.

Post-application monitoring of the soil-water mixtures has been largely limited to pH and fertilizer requirements needed to grow the crop.

Effectiveness of Treatment -- If all of the waste reportedly applied in 1976 (two years prior to our sampling) had been uniformly incorporated into the top 12" of soil over the entire application area and simply accumulated, then observable increases in the application area soil (as compared to the control) would have been expected for Ca, C, N, K, Na, P, and Mg. In fact, among the inorganics, only copper was found in higher concentration in the application area soil than in the control. Organic analysis showed no significant increase of extractable organics in application area soils, suggesting that biodegradation may have occurred. On the other hand, the HRMS data showed the presence of C, H, N and C, H, N, O compounds in both the waste and the application area, but not in the control area. Thus some organic waste components may have persisted in the soil over the period between application and sampling.

With the possible exception of copper, the soil in the application area seems to have been restored to natural background conditions at the time of sampling. Growth of a turf grass crop after waste application may have reduced the concentrations of the primary plant nutrients (N, P, K) in the soil to background levels. The lack of accumulation of Ca, Na, and Mg may be due to the leaching of soluble salts below the zone of incorporation. The increased copper concentration in application area soils is also reflected in increased copper concentrations in application area grasses. Following another year of application of waste at the site, observable increases in zinc might be expected. Both copper and zinc are essential plant (and animal) nutrients, but can be phytotoxic at excessive levels. Such levels have not been reached at Site A, but if further analysis should indicate continued buildup, these elements in the waste could be the parameters controlling the useful life of the site as a waste treatment system.

Potential Environmental Impacts -- Potential for erosion and for contamination of a small stream close to the site is minimal, due to the general topography, the relatively well drained soils, and the growth of vegetation on the site.

Groundwater is found 15-30 feet below the surface of Site A, and was not sampled as part of the present program. The aquifer, however, is considered by State officials to be of major importance as a drinking water source. If there is any migration of waste constituents to ground water, Na^+ is likely to be a leading indicator.

The elevated copper levels observed at Site A do not appear to have had any adverse effects on agronomic activity. However, the potential for accumulation of both copper and zinc could eventually limit continued use of the waste amended soils for turf grass production. At present, there is no established program at the site to monitor for waste components of potential environmental significance, At Site A, these components are principally Cu, Zn and persistent organics in the upper soil layers; and sodium below the zone of incorporation.

Costs -- Since no additional land or equipment was needed at Site A, other than that associated with turf farming, the capital cost associated with landfarming per se is zero. The annual operation costs, associated primarily with transportation and surface application, are about $27,000 or a little over 2¢/gallon of wet sludge applied. It should be noted that these costs would be increased if a monitoring program were initiated to track the fate of potentially problematic waste constituents.

Site B/Plastics Industry Sludge

Physical and Chemical Composition of Wastes Treated -- The waste being landfarmed at Site B is a centrifuged activated sludge from the wastewater treatment system of a plastics manufacturing facility (SIC 3079). The sludge, as applied, contains about 8.5% solids and 91.5% water. Inorganic analyses of the solids fraction yielded the results shown in Table 3. The waste is high in organic carbon, sodium, and the plant nutrients, N, K, and P.

The extractable organics in the waste amounted to 33 mg/L, characterized as follows:

Aliphatic Hydrocarbons, volatile (TCO)	12%
non-volatile (GRAV)	46%
Aromatic Hydrocarbons, non-volatile (GRAV)	7%
Polar Organics, non-volatile (GRAV)	35%

HRMS analysis showed the extractable organics to consist primarily of hydrocarbons with at most one aromatic ring. Fatty acid/ester mass spectral fragments accounted for 24% of the total composition assignments. There were also some indications of the presence of aliphatic sulfur compounds.

Characteristics of the Site as a Waste Treatment System -- Site B is a 180-acre plot owned by the waste generator and leased to local farmers for growing wheat and corn. Soils in the region consist of moderately fine textured silty clay loam and are reported to be well-drained. The small area sampled as part of this program appeared to have a higher proportion of clay soils than did other areas of the farm. The area sampled had a cation exchange capacity of 20.6 - 20.8, and a slightly alkaline pH of 7.3 - 7.5. The topography of the area sampled was nearly level, but rolling hills with 1-3% slopes were more typical of the rest of the farm. Average annual precipitation is about 33 inches, with 70% of it occurring in the

TABLE 3. SITE B WASTE ANALYSIS - TOTAL METALS, T.O.C., AND T.K.N.*

Element	As	B	C	Ca	Cd	Cr	Cu	K	Mg	Mo	N	Na	Ni	P	Pb	Se	V	Zn
Concentrations	4	25	22.93%	660	5	54	60	8200	1600	6.0	2.90%	16.0%	44	6100	50	0.5	4.9	81

* (in μg/g of dried solids, except as noted)

growing season. Mean summer temperatures are about 90°F; average daily minimum winter temperatures are less than 32°F. The frost free period is typically 180-185 days.

Operational Procedures -- Wastes from the manufacturing process are stripped of sulfides, neutralized, and then sent to activated sludge secondary treatment where nitrogen and phosphorous are added. The secondary treatment sludge is centrifuged to increase the solids content in the waste which is landfarmed. Big Wheels® tank trucks are used for both waste transport and application. Sludge is directly injected six to eight inches into the soil via a three-knife subsurface application unit attached to the Big Wheels®. Wastes are applied at the rate of about 7200 gal/acre-yr.

Wastes are incorporated into the soil by standard agronomic procedures, and soils are amended for pH adjustment or with fertilizers, etc., as dictated by the needs of the crop to be grown.

The soil-waste mixtures are analyzed by the farmer for pH, N, P, and K about every two years, and occasionally for organic matter and micronutrients. More extensive analyses are carried out by the waste generator for research purposes. The generator also analyzes a representative sample of the crops grown for Cd, Pb, Zn, Cu and Ni prior to releasing them for sale.

Effectiveness of Treatment -- Wastes had been applied to Site B for two years prior to our sampling, with the latest application having been made 3 months previously. If all wastes applied over the history of the site had simply accumulated, the only elements for which significant increases above background could have been observed are Na, C, and N. In actuality, no significant differences were observed among the elements analyzed between the application and control areas. Nitrogen is almost certainly lost from the soil via plant growth, since the nitrogen fertilizer has been reduced by 20-40 pounds/acre due to waste application. Organic analysis revealed no significant differences between application and control areas. The average electrical conductivity of the upper 12" of the application area (365 μ mhos) was slightly elevated compared to the control area (173 μ mhos).

Wheat plants grown in the application area were taller than those grown in the control area. Analysis of grain for inorganic waste constituents showed no differences between application and control areas.

Potential Environmental Impacts -- Potential for erosion and for surface run-off contamination of a nearby stream is minimal.

Ground water is reportedly at least 60 feet below the soil surface. Soil characteristics favor the build-up of soluble salts in the soil over migration to ground water. However, the potential for migration of sodium salts to aquifers over the long-term does exist.

The waste, as noted earlier, is high in sodium, which is known to have a deleterious effect on soil-plant systems. No impacts have been noted on crops grown to date. If a problem does arise, gypsum may be added to the waste to offset the sodium content or more salt-tolerant crops may be grown.

Costs -- Total capital cost for land, site approval and equipment at Site B is $202,000 in 1978 dollars. Annual operating costs, including capital amortization, come to $40,500/yr or somewhat less than 3¢/gal of wet sludge treated.

Site C/Leather Industry Sludge

Physical and Chemical Composition of Wastes Treated -- The wastes being landfarmed at Site C are sludges from a wet scrubber installed for air pollution control of leather finishing dusts (SIC 3111).

The sludge, as applied, contains about 6% solids and 94% water. Inorganic analyses of the solids fraction yielded the results shown in Table 4. Major elements identified, in order of decreasing concentration, are seen to be organic carbon, N, Cr, Na, Ca, P, K, and Mg.

The extractable organics in the waste amounted to 2200 mg/L, considerably higher than the waste farmed at Sites A and B. The organics in the extract were characterized by liquid chromatography as follows:

Aliphatic Hydrocarbons, volatile (TCO)	3.6%
non-volatile (GRAV)	32.0%
Aromatic Hydrocarbons, volatile (TCO)	1.4%
non-volatile (GRAV)	9.0%
Polar Organics, volatile (TCO)	0.5%
non-volatile (GRAV)	54.0%

HRMS analysis showed the Site C waste to include a higher molecular weight range of hydrocarbons (up to mass 400) than Sites A and B. Among the hydrocarbons are small quantities of polynuclear aromatics. The C, H, N species in the waste are dominated by a high molecular weight series ($C_{24}H_{37}N$, $C_{22}H_{35}N$, etc.). The C, H, O species in the waste are primarily fatty acids (both saturated and unsaturated) with a molecular weight range up to about 400. No organic sulfur species were detected.

Characteristics of the Site as a Waste Treatment System -- Site C is a farm that includes wheat, hay and corn fields as well as a small orchard. Although a variety of tannery wastes have been landfarmed at the site since 1961, the particular field sampled (planted in corn) had had only one waste application, in the spring, three months prior to our sampling.

The field sampled consists of deep, well-drained silt loams. The pH (6.8) is near neutral and the cation exchange capacity (10.3 - 14.2) is moderately high. Although the areas sampled had a gentle slope (<3%), the rest of the farm consists of rolling hills with slopes of 3-8%. Average annual precipitation is about 41 inches, distributed fairly evenly over the year. Average daily maximum summer temperature is about 86°F. Average daily minimum winter temperature is about 26°F. The frost free period averages 194 days.

Operational Procedures -- Waste is transported to the site in a fiberglass lined, 1300-gallon tank mounted on a truck. At the site, the waste is deposited into an unlined holding basin. Settled sludge is periodically removed from the basin with a shovel or front-end loader. It is spread on surface soils to depths up to 6 inches by hand, tractor or manure spreader. Incorporation is carried out via standard agronomic procedures. Post-application monitoring is limited to pH and fertilizer requirements for the farm.

Roughly 3000 gallons of waste had been incorporated into the 1 acre area sampled, about 3 months before our arrival.

Effectiveness of Treatment -- If all of the waste applied had simply accumulated, concentration increases would have been observable in the application area soils for C, N, Cr, Ca, and Na. Increases were ob-

TABLE 4. SITE C WASTE ANALYSIS - TOTAL METALS, T.O.C., AND T.K.N.*

Element	As	B	C	Ca	Cd	Cr	Cu	K	Mg	Mo	N	Na	Ni	P	Pb	Se	V	Zn
Concentrations	0.6	2.4	44.25%	1200	2.8	5600	14	390	360	1.1	8.10%	1300	1.0	937	54	<0.1	5.2	50

* (in μg/g of dried solids, except as noted)

served for C, N, and Cr. Predicted and observed levels of increase are remarkably close, as shown in Table 5. This suggests that no migration of these elements laterally or to a depth of 12" had occurred.

The levels of extractable organics in the application area soils were appreciably higher than the corresponding levels in the control soils. Furthermore, levels in the 0-6" depth samples of the application area were ten times those in the 6-12" depth samples. This suggests that little degradation had occurred in the three-month period between waste application and site sampling. Further evidence is provided by the close correspondence between the organics in the waste and the organics in the application area soils as determined by HRMS analysis. In view of the high molecular weight of the organics and the short time elapsed between application and sampling, little degradation would have been expected.

Potential Environmental Impacts -- These are discussed for Site C as a whole (50 acres) rather than for the small area sampled (1 acre).

Portions of the site contain poorly drained subsoils, and a seasonally high water table that comes within 3 feet of the surface. Small wetland areas occur at several locations throughout the site. Thus the potential exists for wastes to come into direct contact with the ground water, but the impact is unclear.

Chromium had clearly accumulated in the application area soils sampled, and if present in trivalent form as an insoluble oxide, little migration would be expected. On the other hand, corn samples grown in the application area showed small increases in chromium levels, compared to corn grown in the control area. More work is needed on the form(s) of chromium present.

The fate and potential impacts of the organic components of the waste cannot be assessed from the data obtained in this study, because of the short time the waste had been in the soil at the time of sampling. Additional sampling and analysis would have to be done at intervals of several months or more to detect possible degradation.

The farmer uses the waste as a supplementary source of nitrogen and as a conditioner to improve the water retention of the soils. State regulatory authorities also view the sludge as a useful by-product rather than as a waste.

TABLE 5. PREDICTED AND OBSERVED CONCENTRATION CHANGES IN SITE C APPLICATION AREA SOILS

	Element		
	C	Cr	N
Predicted[1]	+1.1%	+130	+1900
Observed[2]	+ .87%	+250	+ 950

1. Predicted concentration change =

$$\frac{[(\text{Kg solids/acre/yr.}) \times (\text{ppm of element in waste})]}{2 \times 10^{6} \text{ kg soil/acre-ft.}}$$

2. Observed mean concentration change =

$$\frac{[(\text{ppm}_{\text{APN 0-6" + APN 6-12"}}) - (\text{ppm}_{\text{CTL 0-6" + CTL 6-12"}})]}{2}$$

Costs -- Capital costs attributable to landfarming at Site C are minimal ($2500). Annualized operating costs come to $4650/yr or a little over 3¢/gallon.

Site D/Petroleum Refining Industry Sludge

Physical and Chemical Composition of Wastes Treated -- The wastes being landfarmed at Site D are sludges from holding ponds, which are part of the wastewater treatment system of a petroleum refinery (SIC 3111).

The sludge, as applied, was reported to contain about 13% solids, 25% oil and 62% water. Inorganic analysis of the solids fraction yielded the results shown in Table 6. The major elemental components in order of decreasing concentration, are seen to be: organic carbon, P, Na, N, Ca, Cr, K, Zn, and Mg. The extractable organics in the waste amounted to 1100 mg/L, characterized as follows:

Aliphatic Hydrocarbons, non-volatile (GRAV)	41%
volatile (TCO)	39%
Aromatic Hydrocarbons, non-volatile (GRAV)	10%
volatile (TCO)	3%
Polar Organics, non-volatile (GRAV)	7%

HRMS analysis showed the presence of a variety of aromatic hydrocarbons, including polynuclear aromatics, small quantities of oxygen and nitrogen containing species, and somewhat larger amounts of sulfur-containing species.

Characteristics of the Site as a Waste Treatment System -- Surface soils on the site range from silty clay to silty clay loam, with clays predominant in upper levels. Soil depths to bedrock vary from more than 60 inches to as little as 10 inches. Soil pH is on the alkaline side (7.8 - 7.9), and cation exchange capacity is high (26.9 - 28.5). This should favor ion exchange and precipitation reactions, which would immobilize heavy metals. Rates of microbial decomposition may be slow due to the limited rainfall (11-14 inches/yr), and generally cool climate (88°F, average daily summer maximum; 10.6°F, average daily winter minimum). The frost free period is 120-125 days.

Operational Procedures -- Wastes are transported by tank truck, from which they are applied to the site surface by gravity flow. Roughly 68,000 gallons of waste had been applied in 1974 to the 1.7 acres that were sampled of the 20 acre site.

Following application, the wet sludge is allowed to dry out on the ground surface over a period of several weeks. The dried wastes are incorporated into the soil to a depth of 5-6 inches with a roto-till. Roto-tilling is repeated at frequent intervals, and fertilizer applications have been made on an experimental basis to increase rates of microbial degradation.

Post-application monitoring includes periodic analyses for the oil content of the soil and classes of organic degradation products.

Effectiveness of Treatment -- Significant increases above background were observed in the application area soils for organic C, Cr, Na and Zn. Significant increases in $SO_4^=$, $C\ell^-$ and electrical conductivity were also observed in application area soils. Interpretation of the results is complicated by the reported presence of a saline seep below the application area soils.

TABLE 6. SITE D WASTE ANALYSIS - TOTAL METALS, T.O.C., AND T.K.N.*

Element	As	B	C	Ca	Cd	Cr	Cu	K	Mg	Mo	N	Na	Ni	P	Pb	Se	V	Zn
Concentrations	105	39	28.24%	1.5%	9.6	1.3%	310	7900	5400	22	2.08%	2.1%	19	3.1%	89	150	39	6500

* (in μg/g of dried solids, except as noted)

The 1973-74 application area 0-6" depth (APN0-6) and 6-12" depth (APN6-12) samples were found to contain 3000 mg/kg and 520 mg/kg respectively of extractable organics. These values are substantially higher than corresponding values for the control area of 140 mg/kg and 89 mg/kg. Thus complete biodegradation had not yet been achieved. However, the APN0-6 sample was found to be much richer in polar organics than the1978 waste, and the enrichment is even larger in the APN6-12 sample. The shift towards polar organics may reflect oxidative degradation of waste components in the soil and possibly some downward migration. On the other hand, the HRMS analysis indicates that a substantial quantity of aliphatic and aromatic hydrocarbons from the waste had not undergone oxidative degradation. Volatile aliphatic and aromatic hydrocarbons appear to have been preferentially lost from the application area. Non-volatile hydrocarbons showed a higher aromatic to aliphatic ratio in the application area samples than in the waste, possibly because of a higher rate of biodegradation of the aliphatics.

Potential Environmental Impacts -- Berms have been constructed around application areas to protect against runoff in a 100-year storm. The surface stream along the northeast border of the site is very high in background dissolved solids (over 20,000 TDS). Ground water may be as much as 200 feet below the surface, and possibly brackish. Site D is in a relatively isolated rural area, more than one kilometer from the nearest area of human habitation. The site is surrounded by a cyclone fence, which prevents access by cattle.

Costs -- Capital costs for land, site approval, and site preparation were $62,500. Equipment is rented, and charged against operating costs. The latter, including capital amortization amount to nearly $13,000/year or a little over 37¢/gallon of waste treated.

Site E/Fabricated Metal Industry Sludge

Physical and Chemical Composition of Wastes Treated -- The wastes being landfarmed at Site E are neutralized pickling liquor sludges from a facility producing fabricated metal products (SIC 349).

The sludge as applied, contains about 20% solids and 80% water. Inorganic analysis of the solids fraction yielded the results shown in Table 7. Among the elements analyzed, the waste is seen to be relatively high in Ca (due to lime neutralization), P, C, K and Mg. Among the elements not analyzed (50% of the dried waste weight), iron would clearly account for a major fraction. The waste is purely inorganic.

Characteristics of the Site as a Waste Treatment System -- The soils range from light silt loam to light silty clay loam. The area sampled was slightly acid (pH = 5.8 - 6.2), and had a moderate cation exchange capacity of 14.9 to 15.3 meq/100 g of soil. Average annual precipitation is around 30 inches, with 40% occurring in summer. The frost-free period is about 150 days.

Operational Procedures -- The lime-neutralized pickling acid waste is transported to the site by tank truck. The waste is either applied to the soil immediately by gravity flow through a stove pipe at the side of the truck, or stored in a clay-lined storage pond for later application. The site has been in use for 5 years. About 600,000 gallons/yr of wet sludge are applied. The most recent application had been one day prior to our sampling visit.

Wastes are applied on a weekly basis, and then incorporated into the soil by a

TABLE 7. SITE E WASTE ANALYSIS - TOTAL METALS, T.O.C., AND T.K.N.*

Element	As	B	C	Ca	Cd	Cr	Cu	K	Mg	Mo	N	Na	Ni	P	Pb	Se	V	Zn
Concentrations	0.2	26	0.12%	3.6%	1	110	92	1800	1400	7	<40	92	30	2.2%	26	<0.1	5	12

* (in µg/g of dried solids, except as noted)

spring tooth harrow after up to three months of surface application. State regulatory authorities require that a phosphate fertilizer be applied to the soil-waste mixture annually.

Monitoring is limited to measuring soil-waste pH three times a year. The results are used to determine the need for additional lime.

Effectiveness of Treatment -- Roughly 600,000 gallons of waste have been applied at the site for 5 years, with the latest application occurring about a day prior to our sampling visit. Elevated concentrations of C, Ca, N, Na and Zn were expected in application area soils compared to controls, and were observed. The observed increases are considerably higher than those predicted on the basis of simple accumulation, however, suggesting that the actual application was larger than estimated by the generator or that the area of application was smaller than that estimated by the site operator, or both.

Potential Environmental Impacts -- Site E is located on a levelled hilltop. Berms have been constructed and the site slope contoured to minimize erosion and surface runoff. Nonetheless, erosion gullies were observed during site visits. Groundwater is located at least 200 feet below the surface. Although the moderate cation exchange capacity would favor immobilization of heavy metals, drastic lowering of the soil pH by application of wastes (from around 6.0 to around 3.6) would promote solubilization and migration. Large increases in electric conductivity (from 250 to 4400 μ mhos) and $SO_4^=$ (from 320 to 38,000) in the application area, compared to the control area, also suggest the presence of soluble salts which can be leached downward below the zone of incorporation.

Costs -- Capital investment for site preparation and equipment was estimated at around \$3500. Operating costs come to \$29,000/yr or a little less than 5¢/gallon.

Site F/Petroleum Refining Industry Sludge

Physical and Chemical Composition of Waste Treated -- The wastes being landfarmed at Site F consist of API separator bottoms and other tank bottom wastes from a petroleum refinery (SIC 2911). The wastes are different in character from those being handled at Site D.

The sludge, as applied, contains about 34% solids, 55% water and 11% oil. Inorganic analyses of the solids fraction yielded the results shown in Table 8.

Organic analysis showed the waste to contain 77 g/L of extractable organics, characterized as follows:

Aliphatic Hydrocarbons, volatile, (TCO)	20%
non-volatile (GRAV)	31%
Aromatic Hydrocarbons, volatile, (TCO)	11%
non-volatile (GRAV)	27%
Polar Organics, volatile (TCO)	8%
non-volatile (GRAV)	4%

HRMS analysis showed the waste extract to contain a wide variety of unsaturated and aromatic hydrocarbons (including polynuclear aromatics), and relatively high molecular weight (200-300) sulfur containing organics, primarily aromatic.

Characteristics of the Site as a Waste Treatment System -- The site is a former wetland, built up with dredge spoil and other types of fill material. The pH is alkaline (7.8 - 8.0) and the cation ion exchange capacity is relatively high (22.9 - 31.7 meq/100 g soil). Average annual precipitation is about 48 inches, distributed fairly evenly throughout the year. The site is located in a warm climate (average

TABLE 8. SITE F WASTE ANALYSIS - TOTAL METALS, T.O.C., AND T.K.N.*

Element	As	B	C	Ca	Cd	Cr	Cu	K	Mg	Mo	N	Na	Ni	P	Pb	Se	V	Zn
Concentrations	8	4	46.46%	8600	2	1600	160	1900	3400	10	0.23%	3000	44	750	93	3	26	1100

* (in μg/g of dried solids, except as noted)

maximum summer temperature of 94°F and average minimum winter temperature of 43°F) and is essentially frost-free year round.

Operational Procedures -- Waste is transported by vacuum tank truck and dumped at one edge of the site. Several telephone poles in tandem, drawn by a tractor, are used to spread the waste over the 7 acre site. Roughly, 1,500,000 gallons/yr of waste have been applied for over ten years.

Following application, the waste is allowed to dry for 1-3 weeks. Incorporation is by rototilling and/or discing. Further discing is done at monthly intervals.

Post-application monitoring is done monthly on the soil-waste mixture. Samples are analyzed for percent oil, percent water, and for 19 heavy metals.

Effectiveness of Treatment -- The site has been farmed intensively for more than 10 years. Application area soils showed higher levels of organic carbon, Ca, Cr, Mo, N, Na, Pb and Zn than control area soils. Increases were also seen in electrical conductivity, $SO_4^=$, and $C\ell^-$ in application areas compared to controls. Organic analysis showed much higher levels of extractable organics in the application area than in the control area, but results are difficult to interpret since wastes had been freshly incorporated one day prior to our sampling visit. A slight enrichment in polar material did indicate that some oxidative degradation had occurred.

Potential Environmental Impacts -- Site F is located in a flat lowland, of significant subsidence. Although very high berms surround the site, there is a potential for flooding and washout in the event of an unusually severe storm.

Application rates have been exceptionally heavy for a long period of time, and the analyses discussed above show significant quantities of waste material down to a depth of 12 inches. Deeper core samples would need to be analyzed to assess the impact potential on groundwater or the nearby estuary.

Costs -- Capital investment for land, site preparation and equipment is estimated at $310,000. Operating costs are about $208,000/yr or slightly over 4¢/gallon.

CONCLUSIONS

No adverse environmental impacts were positively identified at any of the six industrial landfarming sites investigated. However, a number of potential problem areas were found which should be explored via continued sampling and analysis of soil-waste mixtures over time. In sites handling wastes high in salt, the possibility for migration of sodium below the zone of incorporation should be checked.

A great deal of additional work is required on the mechanisms of in situ degradation of organics in soil systems. Such work should include not only the rate of disappearance of the principal organic components of the wastes, but also the identification and rate of formation of intermediate products of degradation.

TOP-SEALING TO MINIMIZE LEACHATE GENERATION

Case Study of the Windham, Connecticut Landfill

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ABSTRACT

After the evaluation of more than 400 landfills, the Windham, CT Landfill was selected for the implementation of a remedial action program. For the present study, SMC-MARTIN drilled additional wells to determine the thickness of the refuse, the depth of the water table under the landfill, the depth to bedrock and ground-water quality. An electrical resistivity survey was conducted in order to define the areal extent of the leachate plume.

Remedial action alternatives evaluated for this site included regrading, revegetation, surface sealing, ground-water cutoff, and plume management. The first three methods proved to be the most cost effective. Suction lysimeters, pan lysimeters, staff gages, and monitoring wells were installed to determine water movement into the landfill and the effectiveness of the remedial measures.

During the summer of 1979, a remedial program was implemented. The site was regraded, gas vents were installed, and 15 cm (6 in) of sand and gravel were emplaced with an additional layer of 10 cm (4 in) of fine-grained sand washings to protect the surface seal. A 20-mil PVC membrane seal was emplaced and covered with 46 cm (18 in) of sand and gravel into which composted sewage sludge and leaves were disced. Revegetation will be accomplished by hydroseeding with a mixture of grasses. Monitoring is being conducted to determine the effectiveness of the membrane seal.

INTRODUCTION

It has been estimated that 15,000 landfills are now operating in the United States. The Resource Conservation and Recovery Act (RCRA) of 1976 requires that landfills not meeting criteria for solid waste disposal facilities and practices be closed within five years. Criteria were promulgated on September 10, 1979 (44 FR 53438) on the basis of which as many as 10,000 of the present operations may be classified as open dumps and may have to be closed. In the actions taken for the closure of these sites and of hazardous waste sites, it is important to implement practices that will minimize or abate the negative environmental effects that the facilities are having. In order to develop and implement a remedial action program at an inoperative waste disposal site, SMC-MARTIN was awarded a contract by the U.S. Environmental Protection Agency.

There are numerous remedial action alternatives that can be used during or after the closure of landfills and dumps. Some of these are passive requiring little or no maintenance after being emplaced. Others are active and require a continuing input of manpower and/or electricity. Techniques for the reduction or elimination of water movement into landfills may be considered in five categories: surface water control, passive ground-water management, active ground-water or plume management, chemical immobilization of wastes, and excavation and reburial. The technologies for these approaches have been widely used in construction, but have not yet been applied to landfill closure. For details concerning remedial action alternatives, see the Fifth Annual Research Symposium of the Solid and Hazardous Waste Research Division.$^{(1)}$

SITE SELECTION

The initial efforts for the project included a site selection process based on criteria established by SMC-MARTIN and EPA. The criteria required that the site have basic engineering and geologic data available; be causing a pollution problem both visible and of concern to the public; be 4 hectares (10 A) or less in size; be inoperative; be geographically accessible to SMC-MARTIN; be able to provide co-funding; be free of current litigation; and be representative of a typical landfill.

Once the site selection criteria had been established, SMC-MARTIN evaluated more than 400 landfill sites in 32 states. Fifty of these sites were inspected by SMC-MARTIN personnel. A total of 15 sites were recommended to EPA as potential candidates for study. After further evaluation and discussion with EPA, five candidate sites were selected. Each of these sites was visited by both SMC-MARTIN and EPA and further evaluation narrowed consideration to three sites. Site investigations and testing indicated that the Windham, CT Landfill would be the site for the implementation of the project.

WINDHAM LOCATION

The Windham Landfill site is located north of Route 6 in the northeastern portion of Connecticut (see Figure 1). It is immediately adjacent to the state-owned and operated Windham Airport (see Figure 2). Drainage from the site is provided by the Natchaug River which flows to the north and west

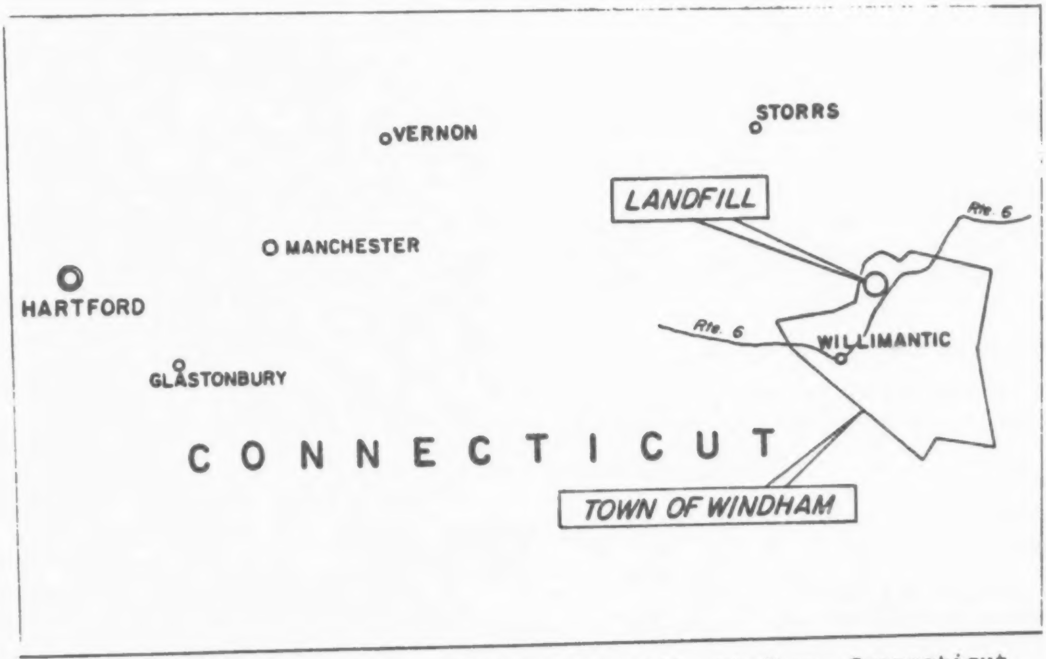

Figure 1. Location of the Windham Landfill, Windham, Connecticut.

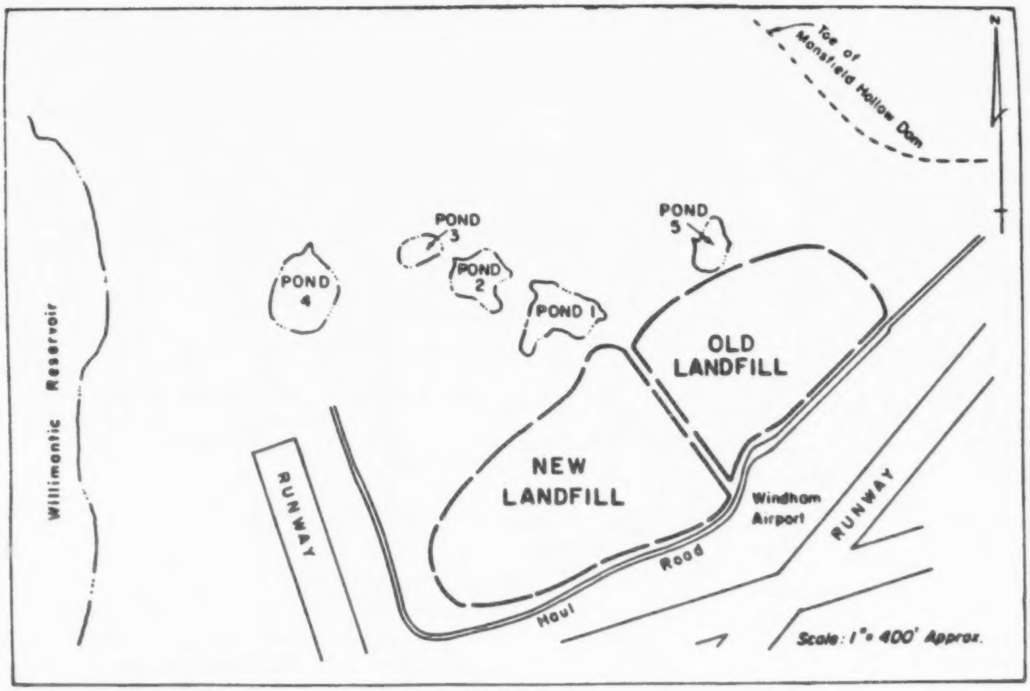

Figure 2. Generalized site plan of the Windham Landfill, Windham, Connecticut.

of the landfill. The U.S. Army Corps of Engineers' Mansfield Hollow Dam is situated on the Natchaug River upstream from the landfill and provides flood control for the area. Immediately downstream from the landfill is the Willimantic Reservoir, a public water supply. The area surrounding the landfill is extremely irregular with numerous water-filled depressions.

WINDHAM LANDFILL OPERATION

The Windham Landfill began operation in the 1940s as an open burning dump in a water-filled depression. When the entire depression had been filled, the Willimantic Redevelopment Authority placed approximately 4.6 to 6.1 m (15 to 20 ft) of demolition wastes over the solid wastes already present in the depression to complete that portion of the landfill.

Filling continued in the western portion of the landfill site initially using the trench method in which solid waste is dumped in depressions excavated above the water table. As filling progressed, the landfill was brought above grade and was changed to an area-type operation. When completed, the landfill was approximately 1.5 to 3.0 m (5 to 10 ft) above local ground surface and occupied approximately 10 hectares (25 A). Medium to coarse-grained sand and gravel was used as cover material.

GEOLOGY

The Windham Landfill is situated in a fine-grained stratified glacial drift. At the surface, the drift is composed of buff colored, medium to fine-grained sand and gravel with pebbles and some cobbles. This material forms a cap for a fine-grained stratified drift deposit which is predominately buff to gray, silty, very fine to fine sand. Depressions (kettles) are common throughout the area of the landfill. Kettles result from ice blocks being buried in outwash from the glaciers which once covered this area. As the ice blocks melted, subsidence resulted, leaving depressions in the ground surface. The eastern (older) half of the Windham Landfill originated as a dump in such a water-filled kettle.

Bedrock in the area is composed of granite gneiss. The bedrock surface dips rapidly from the vicinity of the Windham Airport to the northwest toward the Willimantic Reservoir. According to previous studies, the depth to bedrock ranges from at or near the surface in the vicinity of the Windham Airport to 30.5 m (100 ft) or more in the vicinity of the Willimantic Reservoir.

GROUND WATER

Ground water occurs under water table conditions in the unconsolidated granular deposits of stratified drift surrounding the Windham Landfill.(2) Stratified drift is a highly productive aquifer yielding over 6.3 l/sec (100 gallons per minute, gpm). The average grain size of stratified drift may vary widely. Coarse-grained deposits are found in the valleys in this part of Connecticut. Fine-grained stratified drift deposits occur in association with the coarse-grained deposits yielding appreciably smaller quantities of water.

Ground water at the landfill site occurs at depths of as much as 7.6 m (25 ft). The water table is exposed in ponds lying between the landfill and the reservoir. Ground water moves from the area of the landfill to the west discharging into the Willimantic Reservoir. Mansfield Hollow Lake, north and east of the landfill, and the area to the south of the Reservoir occupied by the airport recharge the ground water.

SITE INVESTIGATIONS

A previous investigation at the Windham Landfill site was conducted under the direction of the Connecticut Department of Environmental Resources in 1975-1976. This study documented the fact that the landfill was contaminating the local ground water which ultimately discharged into the Willimantic Reservoir. As part of this study, a series of eight wells were drilled around the landfill (see Figure 3, Wells #1-8); water samples were collected from these wells and from bodies of surface water. Water elevations in the wells was measured and a water table map was prepared indicating the westward movement of ground water from the landfill toward the Willimantic Reservoir.

Since the western boundary of the plume of contamination emanating from the landfill toward the Willimantic Reservoir was ill-defined, SMC-MARTIN undertook an electrical resistivity survey to further define it and to provide information for the location of additional monitor wells. Subsequent to the electrical resistivity survey, four monitor wells were emplaced to further define the western boundary of the plume of contamination, to determine the depth of contamination from the landfill site, and to further assess the hydrology of the site. The four wells emplaced by SMC-MARTIN during this phase of the study (Wells #9, #10, #11, and #12) were sampled together with selected wells that had been completed as part of the 1975-76 study. The results of chemical analysis confirmed that contamination emanating from the Windham Landfill site was moving toward the Willimantic Reservoir.

Prior to developing the preliminary design for remedial measures for use at the Windham Landfill site, SMC-MARTIN conducted additional hydrogeologic investigations. These included the drilling of Well #13 to conduct an

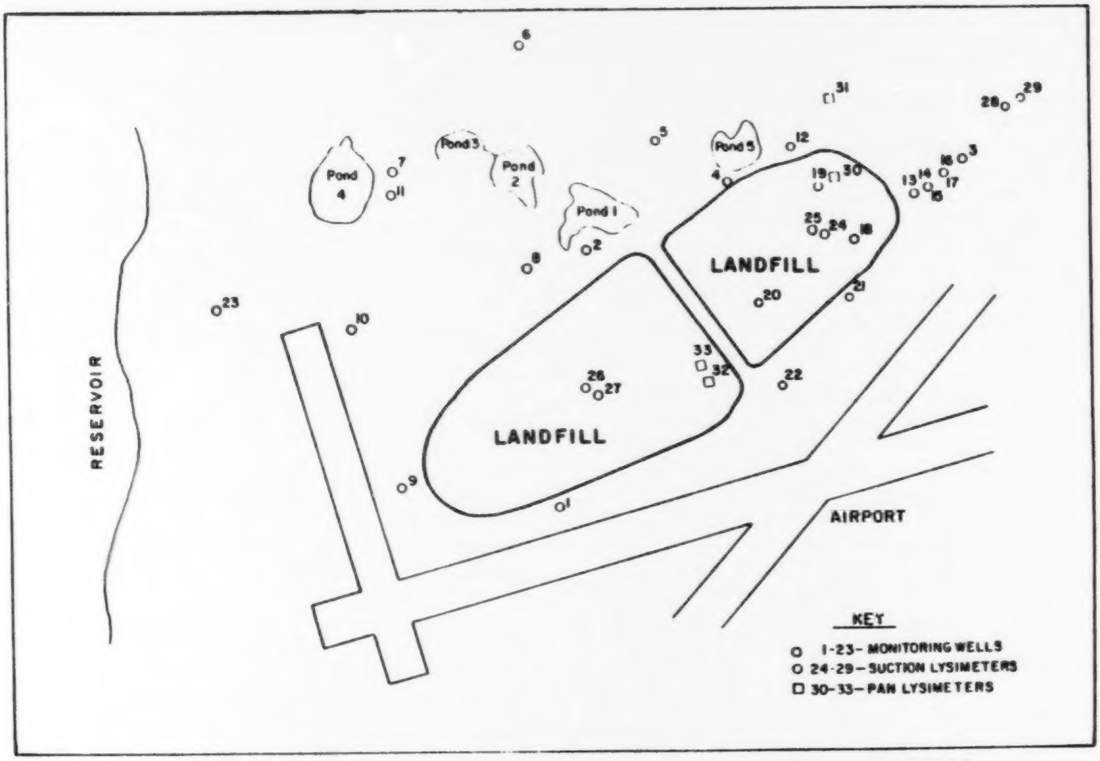

Figure 3. Location of monitoring points at the Windham Landfill, Windham, Connecticut.

aquifer test and drilling additional observation wells (Wells #14 through #22). In this investigation, the nature and thickness of the refuse and its relationship to the local ground-water flow system was assessed in order to determine appropriate remedial measures, their design considerations, and their costs.

The results of this phase of the drilling indicated that the Windham Landfill is situated in a fine-grained stratified glacial drift. Bedrock in the area, composed of granite gneiss, dips rapidly to the northwest toward the Willimantic Reservoir. Figure 4, a cross section through the landfill between Wells #9 and #3, shows that the water table saturates approximately 6.1 m (20 ft) of the older portion of the landfill. The western portion of the landfill is above the water table. The gray fine-grained sand is the aquifer in the vicinity of the landfill. Ground water flows from the airport and the Mansfield Hollow Dam to the landfill and from there toward the Willimantic Reservoir. A 24-hour aquifer test was conducted on Well #13. The influence of the pumping well declined very rapidly in the direction of the Mansfield Hollow Lake since the lake recharges the ground water in the vicinity of the landfill. The major effect of pumpage was found in Wells #14 and #15 immediately adjacent to the pumping well. Wells #18 and #19 were also affected by the pumping because of the lower specific capacity of the refuse through which they were drilled. Given the lack of response from wells located between the landfill and the airport and from those located between the landfill and the ponds, a majority of the water pumped from Well #13 must have come from the direction of the Mansfield Hollow Lake.

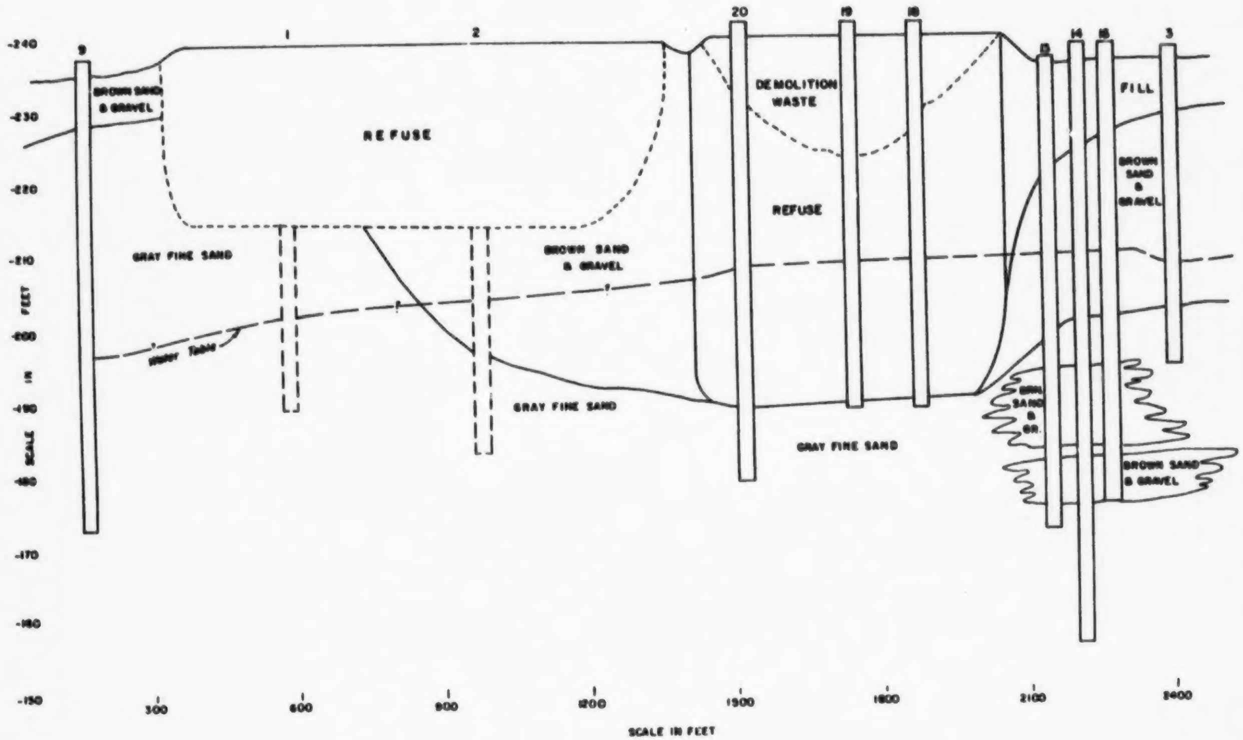
9
1
2
20
19
18
13
14
15
3
BROWN SAND & GRAVEL
REFUSE
DEMOLITION WASTE
REFUSE
FILL
BROWN SAND & GRAVEL
GRAY FINE SAND
BROWN SAND & GRAVEL
Water Table
GRAY FINE SAND
GRAY FINE SAND
BRN. SAND & GR.
BROWN SAND & GRAVEL
-240
-230
-220
-210
-200
-190
-180
-170
-160
-150
SCALE IN FEET
300
600
900
1200
1500
1800
2100
2400
SCALE IN FEET

Figure 4. Cross-section through the Windham Landfill, Windham, Connecticut.

PROPOSED REMEDIAL MEASURES

The Windham Landfill is located in fine-grained sands of moderate permeability; local surface sands and gravel were used for cover material. The eastern half of the landfill extends into the water table and the western half of the landfill is above the water table. Bedrock is at a depth of greater than 33.5 m (110 ft). Ground water moves from the Mansfield Hollow Lake and the area of the airport through the landfill and discharges into the Willimantic Reservoir. A plume of leachate extends from the landfill toward the reservoir.

Remedial actions considered for the landfill included: 1) regrading the completed landfill to increase runoff from the surface, 2) developing diversion ditches to carry surface water away from the area of the landfill, 3) constructing a slurry trench cutoff wall to prevent ground-water movement through the refuse and to lower the water table below the refuse, 4) developing a drainage system to lower the ground-water table in the area of the refuse, 5) counter-pumping to lower the water table below the refuse, 6) covering the landfill with impermeable material to prevent surface water infiltration, 7) revegetating the surface.

The hydrogeologic investigation conducted by SMC-MARTIN refined the alternative remedial measures under consideration. A depth to bedrock of more than 30.5 m (100 ft) below the ground surface would prevent keying a slurry trench cutoff wall into the low-permeability bedrock. Using transmissivity data gathered during the aquifer test, the approximate head loss for slurry trenches of varying depths were calculated. In order to effect a 6.1-m (20-ft) drop in the water table, i.e., to lower it so that it would no longer intercept the landfill, would require a cutoff wall extending 38.1 m (125 ft) into the water table or a total depth of 44.2 m (145 ft). Several approaches were considered in determining the length of a cutoff wall that would dewater the saturated portion of the landfill, reduce ground-water movement through the refuse, or isolate the saturated refuse from the ground water by forming a stagnation cell in the flow system. The first method would require a slurry trench 944.9 m (3100 ft) long x 44.2 m (145 ft) deep at a cost of $3 to $4.5 million. The second method would reduce the flow of ground water through the refuse using a trench 548.6 m (1800 ft) long x 18.3 m (60 ft) deep at an estimated cost of $530,000 to $700,000. The third method would isolate the saturated refuse and provide a further reduction in contamination over Method Two by the construction of a trench 944.9 m (3100 ft) long x 18.3 m (60 ft) deep at an estimated cost of $1 to $1.5 million.

Another alternative ground-water management technique would employ a ground-water drain. This method would use the existing Mansfield Hollow Dam drainage network by extending a subgrade drain around the upgradient end of the landfill. Such a system is commonly used in agriculture and industry to lower water tables from .6 to 2.4 m (2 to 8 ft). In order for the drainage system to be effective, the outlet must be at an elevation lower than the lowest area to be drained. At the Windham Landfill, the lowest outlet is in the northeast corner of the landfill at an elevation of approximately 62.5 m (205 ft). Since the prevailing ground-water levels upgradient of the landfill are between 63.4 and 64.6 m (208 and 212 ft), such a drain would reduce but not eliminate ground-water flow through the landfill.

A third method for controlling ground-water flow through the landfill, counter-pumping, would employ the same technique as that used in the aquifer test but would involve more wells. It was calculated that a ring of 80 wells, 19.8 m (65 ft) deep and surrounding the landfill on 9.1-m (30-ft) centers, would lower the water table approximately 7.0 m (23 ft). A total of 25.2 l/sec. (400 gpm) would be generated by such a system requiring appropriate disposal. An alternate form of this approach would use fewer wells to lower the water table and would form a stagnation cell in the landfill. This would require 18 .3 l/sec (5 gpm) wells approximately 19.8 m (65 ft) deep. The wells would be on 18.3-m (60-ft) centers along the upgradient side of the landfill. The estimated capital cost of the completed dewatering system would have been $160,000. Operation and maintenance costs for such a system would be approximately $14 to $15,000 per year. Added to this would be the cost for the disposal of the contaminated ground water intercepted during the pumping; this could include recycling, direct discharge, treatment, or land application.

It was concluded that the slurry trenches to dewater the landfill or to restrict the movement of ground water would cost from $0.5 million to $4.5 million. A drainage system would not be feasible because of the depth of the water. A counter-pumping program could be designed at a present worth ranging from $125,000 to $380,000 plus disposal costs for the leachate.

After discussion with the Project Officer and the U.S. EPA staff, it was concluded that the most feasible remedial action measures would be to regrade the landfill, cover it with a membrane seal, and revegetate the surface. This would eliminate most infiltration of precipitation into the landfill and would lower the water table in the landfill.

CLOSURE AND MONITORING

SMC-MARTIN was retained by the Town of Windham to prepare closure plans for the landfill that would meet the requirements of the Connecticut Department of Environmental Protection. The closure plan included the regrading of the landfill surface, the installation of a PVC membrane seal over the top of the entire 10 hectares (25 A) site, and the application of up to 46 cm (18 in.) of cover material. Subsequent to the placement of cover, composted leaves and sewage sludge are to be applied in order to supplement the capacity of the cover material to support vegetation. The entire area then will be completely vegetated and the closure procedure completed (see Figure 5).

In the fall of 1978 it was decided that a monitoring program would be implemented to determine the response of the refuse and the underlying ground water to precipitation events. Suction lysimeters were placed in the older area of the refuse to determine the passage of moisture (leachate) through the landfill (Suction Lysimeters #24 and #25, see Figure 3). In the newer part of the landfill, suction lysimeters were emplaced in the refuse and in the earth materials below the refuse and above the water table (Suction Lysimeters #26 and #27). Background suction lysimeters were emplaced adjacent to the landfill to determine moisture movement through relatively undisturbed soils (Suction Lysimeters #28 and #29). In order to determine the quantity of moisture moving through the landfill, four pan lysimeters were emplaced; three with collection areas of .4 m^2 (4 ft^2) and a fourth with a collection area of 2.3 m^2 (25 ft^2) in order to provide cross correlation of data between the smaller and the larger collection areas. Pan lysimeters were installed in the older landfill (Pan Lysimeter #30), in the newer landfill (Pan Lysimeters #32 and #33), and adjacent to the landfill (Pan Lysimeter #31) for background information.

In addition to these suction lysimeters and pan lysimeters, Well #23 was installed (see Figure 3) to collect additional ground-water information immediately downgradient of the landfill

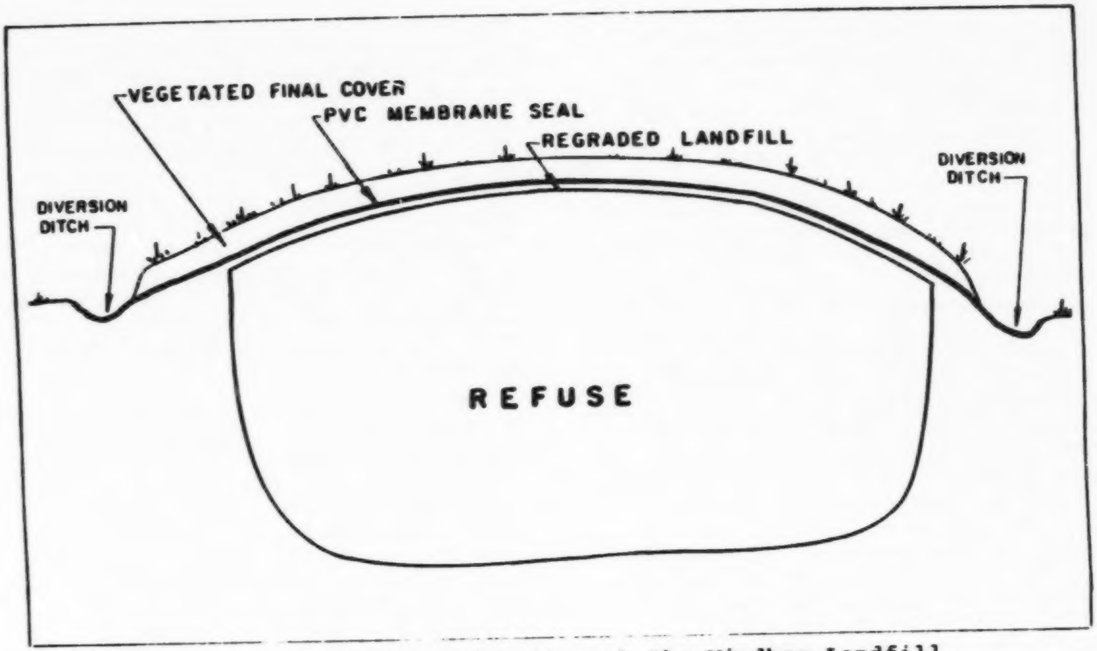

Figure 5. Typical section through the Windham Landfill.

and to define the limit of contamination from the landfill. Staff gages were installed on Ponds #1 and #4 located below the landfill site to determine if the ponds are affected by the stage of the Mansfield Hollow Lake and how they respond to fluctuations in ground-water levels.

Between February and June of 1979, wells, ponds, and lysimeters at the Windham Landfill were sampled on a monthly basis for water quality; water levels in the wells and ponds were measured weekly as was the volume of water collected in the pan lysimeters located on and near the landfill.

Data from this water-sampling program indicated that leachate of moderate strength was generated by the old fill whereas leachate of somewhat higher strength was generated by the newer portion. Leachate was found to affect the ground water downgradient of the fill. There is a significant contrast between the background water quality measured upgradient of the landfill and that found downgradient of the landfill. Analysis of the results of the weekly monitoring of ground-water and surface water elevations and daily precipitation data have verified that significant infiltration is taking place into the landfill. As much as 85 percent of the water passing through the refuse derives from the infiltration of precipitation. The remaining 15 percent of the water represents the presence of ground-water flow through the lowermost portion of the refuse.

IMPLEMENTATION OF A REMEDIAL ACTION PLAN

Contracts were let in the summer of 1979 for regrading the landfill, laying the seal, and applying approximately 46 cm (18 in.) of final cover. Regrading began in August 1979 and was essentially completed by December 1979. The subbase for the seal was excavated from adjacent areas, spread and compacted. It was decided that a 10-cm (4-in.) minimum of fine-grained compacted sand washings would be placed immediately below the seal. This material was emplaced during September and October. A 20-mil PVC seal with solvent weld seams was placed on the site during the period of September through November. It was then covered with a minimum of 46 cm (18 in.) of local sand and gravel which was carefully spread in 15-cm (6-in.) layers. The site had been essentially completed by mid-December 1979. Annual grasses were broadcast on it because of the late completion date. Perennial grasses will be hydroseeded in the spring. A bimonthly program of monitoring was initiated in November 1979 to determine the effectiveness of the seal in preventing the infiltration of precipitation. The suction lysimeters, pan lysimeters, and selected wells will be sampled for the next 24 months.

CONCLUSIONS

The Windham, CT Landfill was selected to demonstrate remedial actions to abate or minimize pollution from closed landfills. The system of remedial actions used at this site included regrading, covering at a minimum depth of 15 cm (6 in.) with local sand and gravel and a minimum of 10 cm (4 in.) of fine-grained sand washings, the application of a 20-mil PVC cover and a final 46-cm (18-in.) vegetated cover. A monitoring system has been installed consisting of suction lysimeters and pan lysimeters to determine the movement of moisture through the refuse, a ground-water monitoring system consisting of wells to determine fluctuations in the water table as well as the rate and movement of leachate in the ground water, and a surface water monitoring system consisting of staff gages in nearby ponds. Monitoring of the landfill has continued for several years establishing complete baseline data, and will continue for two years following the installation of the remedial action alternatives to determine their effectiveness.

ACKNOWLEDGMENTS

This paper addresses one phase of a multiphase project being conducted by SMC-MARTIN under U.S. EPA Contract No. 68-03-2519, Donald E. Sanning, Project Officer. Other phases involved the selection of an abandoned waste disposal site for study; the production of Guidance Manual for Minimizing Pollution from Waste Disposal Sites (EPA-600/2-27-142), a comprehensive discussion of remedial measures and estimates of their costs; the design and implementation of remedial neutralization procedures at the Windham, CT Landfill, and the implementation of a monitoring program to determine the effectiveness of the procedures.

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2. Thomas, M.P., Bednar, G.A., Thomas, C.E., Jr., Wilson, W.E. 1967. Water Resources Inventory of Connecticut, Part 2, Shetucket River Basin. Connecticut Water Resources Bulletin No. 11.

A RESEARCH PROGRAM IN WASTE MANAGEMENT TECHNOLOGY FOR CARBON FIBERS

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In FY 1978 the U.S. Environmental Protection Agency (EPA) began developing a research and development program to address potential problems which may arise from the release of carbon fibers into the environment. The program consists of two parts: Carbon Fiber Characterization and Measurement Technology Development and Carbon Fiber Waste Management Technology Development (Figure 1). The Environmental Sciences Research Laboratory is developing the program for Carbon Fiber Characterization and Measurement Technology. We at the Municipal Environmental Research Laboratory are responsible for the Carbon Fiber Waste Management Technology program. Both of these laboratories are part of EPA's Office of Research and Development and Richard A. Carnes is the Agency's Coordinator for Carbon Fiber Research.

EPA's budget for the first five years of the carbon fiber program is shown in Figure 2. By the end of this fiscal year, it is planned that all funds will be allocated for the characterization and measurement program. The annual funding for the waste management technology development

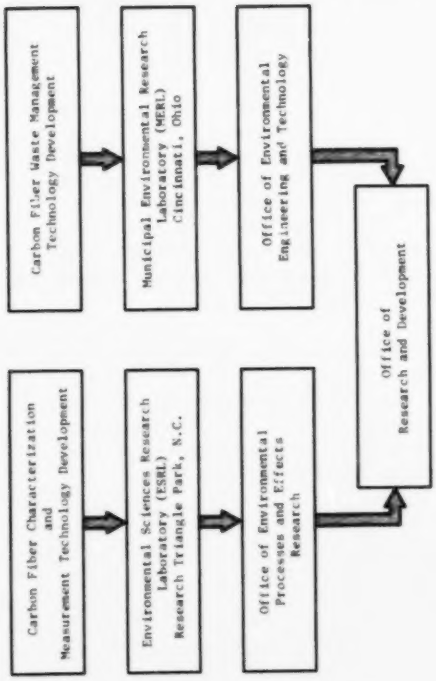
Carbon Fiber Waste Management Technology Development
Municipal Environmental Research Laboratory (MERL) Cincinnati, Ohio
Office of Environmental Engineering and Technology
Carbon Fiber Characterization and Measurement Technology Development
Environmental Sciences Research Laboratory (ESRL) Research Triangle Park, N.C.
Office of Environmental Processes and Effects Research
Office of Research and Development

Figure 1.
EPA's carbon fiber program.

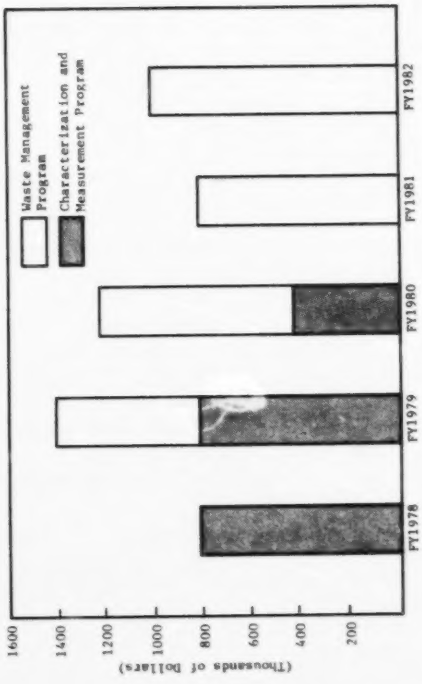

Figure 2.
Five year carbon fiber budget plan.

program is expected to range from $600,000 to $1,000,000 between FY 1979 and FY 1982.

Carbon Fiber Waste Management Technology Development program being carried out by EPA's Municipal Environmental Research Laboratory was initiated in late FY 1979 with technical contracts awarded in three task areas. During FY 1980 and 1981 additional technical contracts will be awarded in four task areas. Long range plans call for further contract awards in five task areas in the FY 1982 period and beyond. The program has three objectives (1) characterization and assessment of the carbon fiber problem, including market penetration studies, (2) development and demonstration of carbon fiber control technology (in the broadest sense, including process changes, etc.) and (3) assessment of the legal, economic and social impacts of carbon fiber regulation and control.

The three tasks which were initiated during late FY 1979 are described below. A complete assessment will be performed by Bionetics of existing information on the environmental implications of the carbon fiber problem including hazards, ambient concentrations and geographical distributions, existing control mechanisms, disposal techniques and risk assessment. The task includes several subtasks. Materials for these subtasks require a close liaison with all programs in other agencies and an incorporation of all pertinent information into the EPA program. The initial subtask is to perform a literature search to identify problems encountered by the release of carbon fiber during handling and disposal, uses of carbon fibers, potential health effects, and information related to the properties, production, manufacture, and resins applications. Based on this literature search, several sets of summary data tables will be prepared. Tables will summarize the type and number of present and/or proposed research military aircraft and transport aircraft which utilize a carbon fiber. Summary tables will be developed for information on carbon fiber manufacturers and their products. The objective of the second subtask is to define risk considerations as interpreted by various Federal agencies, compile their risk assessment programs, and identify areas of concern and data requirements. The third subtask required the preparation of a directory and locator for principal individuals participating in carbon fiber programs (see Appendix 1). Efforts on the fourth subtask are ongoing. The purpose of this subtask is to predict the average concentrations required to cause failure in the types of electrical equipment used for solid waste management; to calculate transfer functions for solid waste management facilities and enclosures for equipment, and; to estimate free fiber characteristics at solid waste locations. Review of present disposal methods is an important part of subtask 5 and accordingly a visit has been made to the refuse incinerator at Saugus, Massachusetts. Finally, a subtask has been undertaken to develop scenarios for carbon fiber life cycles from raw product to ultimate disposal covering the range of potential usage in commerce. Additionally, critical points and potential areas relative to hazards for both individuals and the environment will be defined. We anticipate the completion of all these subtasks early in 1980.

A separate effort has been undertaken by Econ of Princeton, New Jersey. The objective of this effort is the quantification of the current and projected uses of carbon fiber composites in the production of consumer products, evaluation of the potential threats to society from accidental discharge of carbon fibers to the environment and assessment of the economic tradeoffs associated with the use and/or restriction in the use of this material. As this is a 2-year effort the first major results are not expected until late 1980/early 1981.

Researchers at the University of California at Berkeley are working on the assessment of the effects of carbon fiber composite materials in solid waste processing. This task will involve the use of a laboratory scale 10 ton-per-hour shredder, a 3 ton-per-hour continuing system, and associated equipment to investigate the effects of processing solid municipal waste containing projected typical amounts of carbon fiber wastes. The assessment will cover (1) comparison of the processed waste with conventional municipal solid waste, (2) effects of the carbon fiber waste on the processing machinery, including wear and tear and power consumption, (3) evaluation of fugitive dust at various locations in the process, worker exposure and possible pathways to the ambient environment, and (4) preparation of a number of refuse derived fuel (RDF) and densified RDF samples in order to test wear on equipment and power consumption in comparison to conventional solid waste.

Four tasks are programmed to be initiated during FY 1980 or 1981. The task with the highest priority is research on incineration. Combustion tests will be conducted on three types of pilot-scale incinerators comparing emission characteristics of conventional municipal solid waste with municipal solid waste seeded with carbon fiber material. Emission control will be the best available technology for the control of particulate matter for both types of waste. It is the purpose of this study to determine if carbon fiber materials disposed of in the municipal solid waste sector by incineration will pose a potential environmental hazard should incinerator emission contain significant amount of free fibers. Investigation will cover changes in the combustion process itself, characterization of emitted carbon fibers and changes in conventional emissions. Residue from the process will also be carefully analyzed for carbon fiber content.

Three other tasks are planned. The first is an evaluation of carbon fiber waste impacts on existing and emerging disposal and resource recovery systems. This will include a study of trends in the use and application of current and emerging solid waste management technologies, identification of those processes or steps which will receive substantial carbon fiber impact and identification of those most likely to cause significant atmospheric emissions of carbon fiber.

The second is an evaluation of measures to mitigate the impact of carbon fiber on municipal solid waste technologies such as source separation, modification of resins, production changes, modified or partial bans and labeling.

Another task will evaluate carbon fiber discharge test results and determine the adequacy of current and future solid waste processing, recovery and disposal technology to eliminate carbon fiber hazards. This includes identification of technologies which must be modified or newly developed to adequately control discharges, and an estimate of the research and demonstration efforts required.

Tasks to be initiated during FY 1982 or beyond may include:

- Evaluation of the legal, economic environmental, social and political impacts of instituting necessary modifications to current and projected solid waste management systems. These impacts will be evaluated in light of the various risk assessments conducted previously by EPA and other agencies.

- Evaluation of carbon fiber disposal demonstration research in three areas, (1) full-scale incineration studies, (2) RDF and densified RDF combustion, and (3) evaluation of a small particle collection device for controlling carbon fiber emissions.

EPA is pleased to have the opportunity to participate in this meeting as it will help to insure the development of carbon fiber research programs which are compatible with the on-going and planned programs of other organizations. We look forward to working with all of you in the future on this interesting and important environmental program.

APPENDIX 1

DIRECTORY AND LOCATOR
NATIONAL GRAPHITE FIBER PROGRAM
FEDERAL OPERATION OR TASK LEADERS

ENVIRONMENTAL PROTECTION AGENCY

The Municipal Environmental Research Laboratory

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U.S. Environmental Protection Agency
Municipal Environmental Research Laboratory
Cincinnati, Ohio 45268

(513) 684-7871
FTS 684-7871

- Agency coordinator for EPA activities
- Carbon fiber waste management and disposal technology development

The Environmental Sciences Research Laboratory

Dr. J. Wagman
Environmental Protection Agency
Environmental Sciences Research Laboratory
Research Triangle Park, NC 27711

(919) 541-3009
FTS 629-3009

- Coordination of activities for EPA activity with ESRL
- Carbon fiber emission characterization, plus development of monitoring instrumentation and measurement techniques

Dr. Robert Shaw
Mr. Charles Lewis
Environmental Protection Agency
Environmental Sciences Research Laboratory
MD-47
Research Triangle Park, NC 27711

(919) 541-3149/3154
FTS 629-3149/3154

- Development of specialized measurement and analysis techniques for carbon fibers

NATIONAL AERONAUTICAL AND SPACE AGENCY, NASA

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Mr. Richard Fish
NASA Ames Research Center
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Moffett Field, California 94035

(415) 965-5991
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- Alternate Materials Program. Fiber retention by char formation or chemical stabilization of fiber by metal compounds

NASA Langley Research Center

Mr. Robert Huston, Program Manager
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(804) 827-2851
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- Graphite Fiber Risk Analysis Program Office

Dr. S.S. Tompkins
NASA Langley Research Center
Mail Stop 188B
Hampton, Virginia 23665

Dr. S. S. Tompkins

(804) 827-2434
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- Alternate Materials Program. Nonconductive coatings on fibers, hybrid systems, fiber modification by intercalation

NASA Lewis Research Center

Dr. J. Serafini
NASA Lewis Research Center
2100 Brookpark Road
Cleveland, Ohio 44135

(216) 433-4000 Ext. 487
FTS 294-6487

- Alternate Materials Program. Fire resistant resins

DEPARTMENT OF COMMERCE

Office of Basic Industries

Mr. Donald Parsons
Office of Basic Industries
Bureau of Domestic Business Development
U.S. Department of Commerce
Washington, D.C. 20230

(202) 377-4033
FTS 377-4033

- Carbon fiber data base and dissemination of information

National Bureau of Standards

Mr. Denver Lovett
National Bureau of Standards
Building 202, Room 216
Washington, D.C. 20234

(301) 921-3828
FTS 921-3828

- Evaluation of consumer electrical and electronic equipment (also support to Graphite Fiber Risk Analysis)

DEPARTMENT OF DEFENSE AND DEFENSE CIVIL PREPAREDNESS

Lt. Col. Lawrence Abramson
Director
Ballistics Research Laboratory
USA AVRADCOM Attn: DRDAR-BLC-HN
Aberdeen Proving Ground, Maryland 21005

(301) 278-3086
FTS 922-3311
(Baltimore)

- Chief JTCG

U.S. Air Force Coordination and Direction of Activities

Mr. Quentin Porter
Commanding Officer
Rome Air Development Center/RBTC
RAPCIRB
Griffiss AFB, New York 13441

(315) 330-3061
FTS 952-3061

U.S. Army Coordination and Direction of Activities (Efforts now terminated)

Dr. L. R. Vande Kieft
Director
Ballistics Research Laboratory
USA AVRADCOM Attn: DRDAR-BLT-HN
Aberdeen Proving Ground, Maryland 21005

(301) 278-2632
(301) 278-2528
FTS 922-3311
(Baltimore)

U.S. Navy Coordination and Direction of Activities

C. E. Gallaher
Naval Surface Weapons Center
Attn: Code CF 56
Dahlgren, Virginia 22448

(703) 663-8136
FTS 937-6011
(Roanoke)

Defense Civil Preparedness Agency

Mr. Thomas Boven
Defense Civil Preparedness Agency
Staff College
Federal Center
Battle Creek, Michigan 49106

(616) 962-6171
FTS 372-6171

- Technical information and briefing to local governments. Fire, police emergency services procedures for handling a carbon fiber fire release incident
- Data and record compilation and analysis

for carbon fiber fire release incidents

DEPARTMENT OF ENERGY

Mr. Thomas Garrity
Division of Electric Energy Systems
Energy Research and Development Admin.
200 Massachusetts Avenue, NW
Washington, D.C. 20545

(202) 376-4595
FTS 376-4595

- Effects of airborne fibers on power generation and distribution equipment

DEPARTMENT OF HEALTH, EDUCATION AND WELFARE

Dr. Ralph Zumwalde
U.S. Public Health Service
Robert A. Taft Laboratories
4676 Columbia Parkway
Cincinnati, Ohio 45226

(513) 684-3255
FTS 684-3255

- Carbon fiber environment studies
- Morbidity mortality studies on exposure to other fibrous materials (continuation of existing programs as basis for comparison)

DEPARTMENT OF LABOR

Dr. R. Hays Bell
Department of Labor
OSHA
200 Constitution Avenue, NW
Room N-3651
Washington, D.C. 20210

(202) 523-7031
FTS 523-7031

- Review and comparison analysis relative to development of a regulation for carbon fiber exposure in a worker environment

DEPARTMENT OF STATE

Mr. R. Reckmales
Department of State
OES/APT/SA
Room 4333
Washington, D.C. 20520

(202) 632-5071
FTS 632-5071

- International coordination and dissemination of carbon fiber related data or information

DEPARTMENT OF TRANSPORTATION

Transportation System Center, Cambridge, Massachusetts

Dr. Karl Hergenrother
Transportation Systems Center/521
Kendall Square
Cambridge, Massachusetts 02142

(617) 494-2696
FTS 837-2696

- Carbon Fiber Studies Project Office

The Federal Aviation Administration

Mr. Arnold E. Anderjaska
Federal Avaiation Administration
AWS 120
800 Independence Avenue
Washington, D.C. 20546

(202) 426-8382
FTS 426-8382

- Coordination of accident data involving carbon fiber on civil aircraft
- Notification of incidents involving carbon fiber release from civil aircraft

CENTRAL INTELLIGENCE AGENCY

Mr. Chester Schuler
Central Intelligence Agency
OSI
Washington, D.C. 20505

(703) 351-6306
FTS (202) 351-6306

- Coordination of information for the CIA

GENERAL ACCOUNTING OFFICE

Mr. C. Boykin
General Accounting Office
Room 2220 Annex, SSA
Woodlawn, Maryland 21235

(301) 594-4430
FTS 934-4430

- General program review

OFFICE OF MANAGEMENT AND BUDGETS

Dr. K. Mohan
Office of Management and Budget
Room 8002
New Executive Office Building
Washington, D.C. 20503

(202) 395-3935
FTS 395-3935

- Allocations of financial resources and budget planning

OFFICE OF SCIENCE AND TECHNOLOGY POLICY

Col. Wayne Kay, Director
Mr. Benjamin Huberman, Deputy
Office of Science & Technology Policy
Old Executive Office Building
Room 483
Washington, D.C. 20500

(202) 395-3272
FTS 395-3272

- Overall direction, coordination and control monitor for the Carbon Fiber Action Plan